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INVESTIGATION OF THE DEGREE OF DISPERSION OF PEAT SUSPENSIONS WITH THE AID OF THE SEDIMENTOMETER AND THE ELECTRON MICROSCOPE

M. P. Volarovich and N. V. Churaev

The question of the degree of dispersion of peat is a very important one in relation to the technology of its winning, processing, and drying. However, very few papers have been published on this question up to the present time. The only studies known are those of Semensky and Rivkina [1], Dumansky and coworkers [2], Volarovich and Kuzminskaya [3], and Rakovsky and Rakovskaya [4]. It was of interest to obtain graphs for the particle size distribution of highly disperse peat suspensions, that is, for the so-called peat water, obtained after settling of the coarsely disperse fraction of peat.

Three samples of peat water were studied, obtained from B. F. Sergeev (Peat Experimental Station), and with dry material content (c) of 0.113, 0.078, and 0.076%. Each sample was represented by two suspensions: original and coagulated. 5% solution of aluminum sulfate was used to coagulate the samples. Thus, the amount of coagulant per 1 g of the dry peat material was greatest for the suspension with $c = 0.076\%$ and least for the suspension with $c = 0.113\%$.

The degree of dispersion of peat suspensions was studied with the aid of a gravimetric sedimentometer [5], which was a modified form of Figurovsky's apparatus [6]. To avoid orthokinetic coagulation, the suspensions were diluted with distilled water to a concentration of 0.02-0.03% of the dry substance during the analysis. The fact that the density of peat particles of different dimensions varies was taken into account in calculations of the equivalent particle radius by Stokes' formula. The larger particles, containing a considerable amount of water, have low density in comparison with the small particles. Thus, the density of particles of the order of 50-100 μ in size is only 1.06-1.03 g/cm³, while the density of particles less than 2 μ in size is equal to the density of absolutely dry peat, namely 1.4 g/cm³. These values, as well as intermediate values, were obtained from observations of the rate of fall of particles of peat suspensions with the aid of a microscope with a micrometer eyepiece.

Fractions with particle size less than 0.25 mm were subjected to sedimentometric analysis; fractions with particles larger than 0.25 mm were divided by sieves with mesh hole diameters of 3, 1, and 0.25 mm.

Figures 1, 2, and 3 show the size distribution curves of the particles in the original and coagulated suspensions, determined by sieve and sedimentometric analysis. The abscissa axis shows the particle radius in microns, on a logarithmic scale, while the ordinate axis shows values of the distribution function $r \frac{dm}{dr}$. The area embraced by the distribution curve on the scale shown in the graphs corresponds to 100% of the mass of the particles in the suspension. The sedimentometer gives size distribution from 250 to 1 μ . The mass of the fraction with particle radius less than 1 μ was determined as a total, and is expressed by the area of the rectangle the base of which corresponds to the radius range of 0.5-0.05 μ . It is shown below that it is possible to stop at a particle radius of 0.05 μ .

Examination of the graphs in Fig. 1 and 2 leads to the conclusion that in the suspensions studied only the highly disperse fraction with particle size less than 1 μ is coagulated. As a result of the coagulation, the finely disperse fraction forms aggregates of a sufficiently stable particle size. When the amount of coagulant per 1 g of

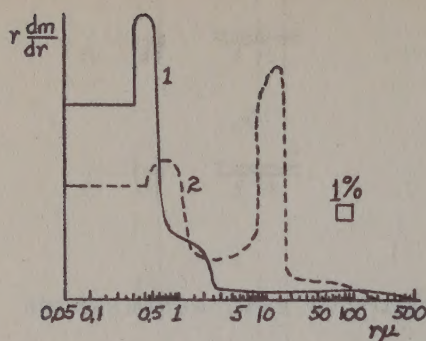


Fig. 1. Particle size distribution curves, obtained with the sedimentometer for peat water with a concentration of 0.113% of the dry substance: 1) original; 2) coagulated suspension.

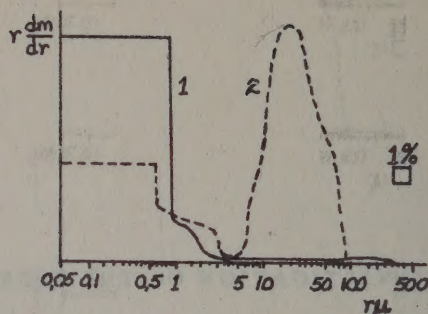


Fig. 2. Particle size distribution curves, obtained with the sedimentometer for peat water with a concentration of 0.076% of the dry substance: 1) original; 2) coagulated suspension.

the dry substance is less, the dimensions (equivalent diameters) of the main mass of the aggregates vary from 16 to 32 μ (Figure 1), while at higher coagulant concentrations (Figure 2) the range of spread of the aggregate size is considerably wider (from 12 to 140 μ), but most of the aggregates are from 20 to 50 μ in size.

While peat water with original concentration of 0.113 and 0.076% mainly consisted, as Fig. 1 and 2 show, of a finely dispersed fraction, the peat water with 0.078% concentration contained considerable amounts of coarse fractions (Fig. 3). Comparison of the curves for the original and coagulated states of this suspension shows that the coarsely dispersed fractions of the suspension do not coagulate, and the coagulant affects only the highly dispersed fraction.

From the distribution curves for the original and coagulated suspensions it is possible to calculate the amount of the finely dispersed fraction which coagulates and forms aggregates, and the amount which is not affected by the coagulation. The content of the fraction of particle size less than 2 μ was taken as 100% in the original suspension. Calculation shows that in the suspension with $c = 0.113\%$, 33% of the particles less than 2 μ in size, and in the suspension with $c = 0.076\%$, 58% of such particles are coagulated. The difference in the "scope" of the coagulation is explained by the higher concentration of coagulant in the second suspension. The concentration of coagulant relative to the amount of dry substance was 1.5 times as great in the suspension with $c = 0.076\%$ as in the suspension with $c = 0.113\%$, and hence the scope of the coagulation increased by a factor of 1.75.

There is a certain discrepancy in the case of the suspension with $c = 0.078\%$ (Fig. 3). In this case only 9% of the fraction below 2 μ is coagulated, although the coagulant concentration was fairly high. This may be explained by the fact that part of the coagulant is adsorbed by the coarsely dispersed fraction, which lowers the amount of coagulant available for the finely dispersed fraction.

A great interest is presented by the distribution curves for particle sizes below 1 μ , that is, the region of colloidal particles of a high degree of dispersion, represented on the graphs by the area of a rectangle. It should be noted that the overwhelming majority of the particles in the original suspensions of 0.113 and 0.076% concentration lies in this region. It might be possible to attempt to study this region with the aid of the gravimetric sedimentometer, by increasing the sedimentation time from 2.5 (in the accepted method) to 25-30 days. However, apart from the duration of such analysis, the use of sedimentometric analysis for particles less than 1 μ in diameter is not sufficiently reliable. The small size and low density of the peat particles make them sensitive to convection currents and Brownian movement. Figurovsky [6] considers the upper limit of applicability of sedimentometric analysis to be a particle size of $\sim 0.5 \mu$ at a density of 2.5 g/cm³. For peat particles of lower density this limit should be increased. It should also be noted that prolonged standing (25-30 days) of the suspension in the sedimentometer may lead to aggregation of the particles as the result of coagulation, which would distort the results of the analysis.

For the analysis of highly dispersed fractions, photographs of four suspensions were taken with the aid of the

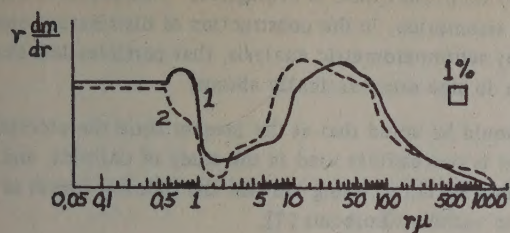


Fig. 3. Particle size distribution curves for peat water with a concentration of 0.078% of the dry substance:

1) original; 2) coagulated suspension.

microscope, and a grey background formed by particles in the second and third plane. Only the particles in focus were counted, the outlines of which were sufficiently sharp and for which there was no doubt about possible overlapping by other particles. The results of the measurements and calculations are shown in the Table.

Treatment of the Results of Electron Microscope Analysis of the Original Suspension

Fraction size, μ	Number of particles Δn	Mass of the particles, $\Delta m \cdot 10^{-12}, g$	Percentage content, p
Concentration of dry substance 0.113%			
1.00-0.75	6	2.940	18.40
0.75-0.50	30	5.350	33.10
0.50-0.25	85	3.290	20.36
0.25-0.10	37	0.390	2.41
<0.10	42	0.004	0.03
Total...	200	11.974	74.10
Concentration of dry substance 0.076%			
1.80-1.00	4	5.7200	31.70
1.00-0.60	19	6.8300	37.80
0.60-0.40	42	3.8500	21.40
0.40-0.20	38	0.7500	4.15
0.20-0.10	24	0.0600	0.33
0.10-0.05	19	0.0060	0.033
<0.05	12	0.0001	0.0005
Total...	158	17.2161	95.4135

mentometric, and electron-microscopic analysis, shown in Fig. 6. The coordinates and scale of the graphs are the same as in the distribution curves in Fig. 1, 2, and 3.

It should be noted that despite the use of three different methods of dispersion analysis, smooth distribution curves are obtained, which indicates that the methods used are sufficiently accurate. This is also supported by the fact that the order of the size of the aggregates shown in the Photographs 4 b and 5 b agrees with the order of size obtained by sedimentometric analysis. Thus, in conjunction with sieve and sedimentometric analysis it is possible with the aid of the electron microscope to obtain complete distribution curves for polydisperse suspensions.

Examination of the complete distribution curves for the original suspensions with $c = 0.113\%$ and $c = 0.076\%$ leads to the conclusion that the main mass of the particles in the colloidal portion of peat are of the order of 0.5-1.0 μ in size, as the distribution curves show a clearly defined maximum in this region. Despite the fact that the

electron microscope*. Fig. 4 and 5* show electron micrographs of the original and coagulated suspensions with concentrations of 0.113 and 0.076%, at a magnification of 4000. For convenience of subsequent treatment of the photographs, these were further enlarged 2.75 times by a photographic method; thus, the total magnification was 11,000.

Particles less than 1 μ in size were counted and measured on the photographs of the original suspensions. However, some care had to be taken in counting and measuring the particles, as overlapping and obscuring of particles in the photographs was possible. Examination of the photographs shows sharply defined dark particles which lie in the focus of the electron

The Table was compiled from counts and measurements of particles in two photographs of different regions of the same suspension. The mass of the particles, Δm , was calculated from the usual formula. The total percentage content of the fine fractions (74.1 and 95.4%) was determined from sedimentometric results. The values of $p\%$ for the fractions were found by proportional division by values of Δm .

The percentage contents p of the fractions, obtained by these calculations, were used to plot particle size distribution graphs based on data from sieve, sedi-

* The electron microscope photographs were taken by V. I. Aleksashin, assistant in the Department of Physics of the V. M. Molotov Institute of Mechanization and Electrification, to whom the authors express their sincere gratitude.

** See plate, page 309.

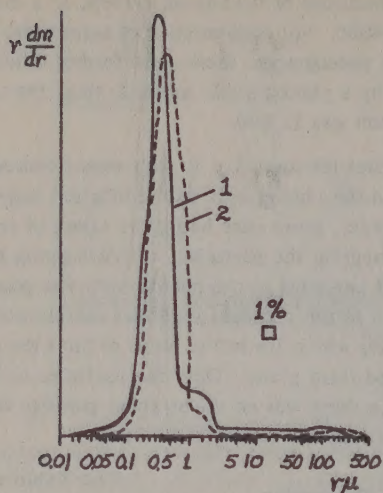


Fig. 6. Complete particle size distribution curves for the original peat water with dry contents: 1) 0.113%; 2) 0.076%, found with the sedimentometer and the electron microscope.

number of particles less than 0.1μ in size is relatively great (see Table) their total mass is negligible. This provides a basis for the assumption, in the construction of distribution curves obtained by sedimentometric analysis, that particles less than $0.1-0.05 \mu$ in size are practically absent.

It should be noted that at the present time the electron microscope is successfully used in the study of colloids, and, in particular, for determining the size distribution curves of the pores in various adsorbents [7].

Examination of electron microscope photographs of peat also permits investigation of the structure of the particle in the colloidal fraction. From the Photographs 4a and 5a it may be concluded that the particles of the colloidal fraction of peat are in most cases rounded and approximate to a spherical shape; no lamellar structure is found, as otherwise, as the result of random orientation, at least part of the particles in the sample would appear in the photographs as elongated ellipses or rods. The blackness of the particles, which is evidence of sufficient density of the substance, also indicates their spherical form. The same observation also shows absence of visible internal porosity of the particles. Their external porosity is also not great: the particles have fairly sharply defined outlines without visible irregularity (naturally, only those in the focus of the electron microscope).

An entirely different appearance is presented in Photographs 4b and 5b by the aggregates of particles, obtained as the result of coagulation. These are loose formations with extensive internal and external porosity as the result of incomplete cohesion of the particles. The pore dimensions are of the same order as those of the particles forming the aggregates, $0.5-1.0 \mu$. In view of the large size of the aggregates, which do not fit completely into the field of the photographs, it is difficult to say anything about the shape and the direction of growth of the aggregates. However, the gradual blackening of the aggregate images from the edges to the center of the photographs leads to the supposition that the aggregates, like the particles, have a shape close to spherical.

SUMMARY

1. In the coagulation of peat water by a 5% solution of aluminum sulfate, the colloidal fraction of the peat, with predominant particle size of $0.5-1.0 \mu$, coagulates and chiefly forms aggregates of sufficiently stable dimensions of 16 to 50μ . The effect of the coagulant is not noticeable in the coarsely dispersed portion of the peat water. The intensity of coagulation increases with increase of the coagulant concentration relative to the dry peat content.

2. By combination of sieve analysis (fractions with particles greater than 250μ) and sedimentometric analysis (fractions $250-1 \mu$) with electron microscopy, (fractions less than 1μ) it is possible to obtain complete particle size distribution curves for polydisperse suspensions.

3. The colloidal fraction of peat water consists to a large extent of particles $0.5-1.0 \mu$ in size, close to spherical in shape, and without any appreciable internal or external porosity. The aggregates formed as the result of coagulation have considerable internal and external porosity.

Moscow Peat Institute

Received February 10, 1954.

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EFFECT OF SELECTIVE WETTING ON THE PROCESS OF EMULSION FORMATION

R. M. Dvoretzkaya

Effect of Solids on the Type of Emulsion Formed. As was shown by our results in the earlier investigations, the type of emulsion formed is affected by the selective wetting of the walls of the vessel by the liquid. The type of emulsion is determined by the interaction between the liquid and the solid surface relative to which the displacement of the liquids takes place. If the liquid effectively wets a given surface and, which is particularly important, is firmly retained on it in the form of a layer, then such a liquid does not break up into separate drops during stirring, and becomes the dispersion medium of the emulsion. Thus, the distribution of the liquid into separate drops apparently takes place at the surface of the solid present in the system during stirring.

The following experiments were carried out to elucidate this problem. Equal volume of the liquids were poured into a glass cylinder, washed clean, and the liquids were then mixed with the aid of a plunger or by air supplied through a tube.

The mixing was carried out in a glass cylinder, but with different plungers: made of glass and of plastic (Plexiglass). The tubes through which the air for mixing was supplied were also made from these materials. The results of the experiments are shown in Tables 1 and 2.

TABLE 1
Effect of Selective Wetting on the Type of Emulsion Formed. *

Aqueous phase	Kerosene		Transformer oil	
	glass plunger	plastic plunger	glass plunger	plastic plunger
Distilled water	o/w	w/o	o/w	w/o
Sodium oleate 0.1 N	o/w	w/o	o/w	w/o
Sodium oleate 0.03 N	o/w	w/o	o/w	w/o
Sodium naphthenate (M = 350) 0.01 N ..	o/w	w/o	o/w	w/o
Sodium naphthenate 0.05 N	o/w	w/o	o/w	X
Sodium sulfonates 0.1%	o/w	w/o	o/w	w/o
Sodium sulfonates 2%	o/w	o/w	o/w	o/w

TABLE 2
Effect of Selective Wetting on the Type of Emulsion Formed.

Aqueous phase	Pétroleum	
	glass tube	plastic tube
Distilled water	o/w	w/o
Oil well water, 1	o/w	w/o
Oil well water, 2.	o/w	w/o
Sodium sulfonates, 0.05%	o/w	w/o
Sodium sulfonates, 0.1%	o/w	w/o
Sodium sulfonates, 0.2%	o/w	X
Sodium sulfonates, 2%	o/w	o/w

As the data of Tables 1 and 2 show, it is possible to change the type of emulsion formed merely by changing the material of the plunger or tube. When the mixing is effected in a glass cylinder with a glass plunger, o/w type emulsions are formed; if the same liquids are mixed in the same cylinder but with a plastic plunger reverse emulsions, of the w/o type, are formed. The same

is found for glass and plastic tubes when the mixing is done by means of air.

The presence of solids in the volume of the liquid also affects the type of emulsion. Emulsions were prepared by mixing the liquids by means of a glass tube in a glass cylinder, but before mixing 2% of small pieces of plastic

* Note. In this and the following Table, w/o = emulsion of the water in oil type; o/w = oil in water; x = both types of emulsion.

TABLE 3

Effect of Selective Wetting on the Type of Emulsion Formed with Small Pieces of Plastic Added to the Oil

Aqueous phase	Kerosene		Transformer oil	
	without plastic	with plastic	without plastic	with plastic
Distilled water	o/w	w/o	o/w	w/o
Sodium oleate 0.01 N	o/w	w/o	o/w	w/o
Sodium oleate 0.03 N	o/w	w/o	o/w	w/o
Sodium naphthenate (M = 350) 0.01 N	o/w	w/o	o/w	w/o
Sodium naphthenate 0.05 N	o/w	w/o	o/w	w/o
Sodium sulfonates 0.1%	o/w	w/o	o/w	w/o
Sodium sulfonates 0.2%	o/w	w/o	o/w	X
Sodium sulfonates 2%	o/w	o/w	o/w	o/w

TABLE 4

Effect of Selective Wetting on the Type of Emulsion Formed on the Addition of Pieces of Plastic and Gumbrin to the Oil

Aqueous phase	Petroleum		
	without plastic	with plastic	with spent gumbrin
Distilled water	o/w	w/o	w/o
Oil well water, 1	o/w	w/o	w/o
Oil well water, 2	o/w	w/o	w/o
Sodium sulfonates 0.05	o/w	w/o	w/o
Sodium sulfonates 0.1%	o/w	w/o	w/o
Sodium sulfonates 0.2%	o/w	o/w	w/o
Sodium sulfonates 2%	o/w	o/w	X

TABLE 5

Properties of the Petroleum Used in the Experiments

Specimens	Specific gravity at 20°	Kinematic viscosity at 20° in centistokes	% tars (official Excise test)
1	0.8565	14.9	20
2	0.8705	19.6	17
3	0.8885	48.6	30

were added to the oil, and in the case of petroleum, spent bleaching clay (gumbrin) was also

added, after previous soaking overnight in a separate portion of the same petroleum to extract part of the resinous substance (the gumbrin was thus transformed into a hydrophobic substance). For the results of these experiments see Tables 3 and 4.

In the absence of plastic, the effect of the glass tube and walls of the cylinder resulted, as usual, in the formation of o/w emulsion. If a sufficient number of solid particles, well wetted by the oil, was added during mixing, emulsions of the w/o type were formed. Each such particle retains layers of oil around itself and does not allow them to separate as isolated drops.

The results obtained with 2% solutions of sodium sulfonates are of interest. As was shown earlier [1], these detergents have a high wetting power and wet the plastic well. When 2% solutions of these substances are mixed with kerosene, transformer oil, and petroleum, w/o emulsions are not formed either with the use of a plastic plunger or tube, or in presence of pieces of plastic in the oil. In this case the plastic surface is wetted so well by the aqueous phase that only emulsions with water as the dispersion medium are formed.

The effect of selective wetting on the type of emulsion, in the case of solids, was noted by several workers. However, in all cases, this effect was studied only in relation to the ability of the emulsifier to be retained at the boundary between two liquids.

Which liquid selectively wets the given solid emulsifier determines the type of emulsion.

However, as Rebinder and Pospelova indicate [2], this selective wetting of the particles cannot be complete, as in complete wetting these particles would remain within the bulk of one of the liquids without adhering to the droplet surfaces, and so could not affect the type of emulsion.

From our experiments, however, it follows that the formation of an emulsion of a given type is affected by solid particles which are subject to complete selective wetting by one medium only. Thus, in presence of a pure glass surface o/w emulsions are formed, while in presence of particles of plastic w/o emulsions are formed. Because of the complete wetting of the particles by one of the liquids they do not adhere to the surface of the droplets formed, and the resultant emulsion is unstable. If, however, the particles of the substance have on their surface certain structural elements selectively wetted by the disperse phase, that is, if they are able to adhere to the droplet

TABLE 6

Specific Gravity and Composition of the Oil Well Waters Used in the Experiments

Specimens	Specific gravity at 20°	Content, %					
		Ca	Mg	Cl	SO ₄	HCO ₃	CO ₃
1	1.0907	0.491	0.162	7.200	0.033	0.046	—
2	1.0131	0.002	0.002	0.482	0.004	0.470	0.089

TABLE 7

Effect of Selective Wetting on the Type of Emulsion Formed

Oil phase	Aqueous phase	Glass		Iron	Plastic
		2 min.	60 min.	0.5 min.	0.5 min.
Petroleum 1	Distilled water	o/w	o/w	w/o	w/o
Petroleum 1	Oil well water, 1	o/w	o/w	w/o	w/o
Petroleum 1	Oil well water, 2	o/w	o/w	w/o	w/o
Petroleum 2	Distilled water	o/w	o/w	w/o	w/o
Petroleum 2	Oil well water, 1	o/w	o/w	w/o	w/o
Petroleum 2	Oil well water, 2	o/w	o/w	w/o	w/o
Petroleum 3	Distilled water	o/w	o/w	w/o	w/o
Petroleum 3	Oil well water, 1	o/w	o/w	w/o	w/o
Petroleum 3	Oil well water, 2	o/w	o/w	w/o	w/o
Transformer oil	Distilled water	o/w	o/w	w/o	w/o
Transformer oil	Oil well water, 1	o/w	o/w	w/o	w/o
Transformer oil	Oil well water, 2	o/w	o/w	w/o	w/o

TABLE 8

Effect of Addition of "Kontakt" to the Aqueous Phase on the Type of Emulsion Formed

Oil phase	Aqueous phase	Iron	
		0.5 min.	60 min.
Oil 1	Oil well water 1	w/o	w/o
Oil 2	Oil well water 1	w/o	w/o
Oil 3	Oil well water 1	w/o	w/o
Oil 1	Oil well water 1 + 0.5% of sodium sulfonates	o/w	o/w
Oil 2	Oil well water 1 + 0.5% of sodium sulfonates	o/w	o/w
Oil 3	Oil well water 1 + 0.5% of sodium sulfonates	o/w	o/w
Oil 1	Sodium sulfonates 2%	o/w	o/w
Oil 2	Sodium sulfonates 2%	o/w	o/w
Oil 3	Sodium sulfonates 2%	o/w	o/w
Oil 1	Calcium sulfonates 2%	o/w	o/w
Oil 2	Calcium sulfonates 2%	o/w	o/w
Oil 3	Calcium sulfonates 2%	o/w	o/w

surfaces, then the latter will become covered with a protective coating of solid particles and the emulsion formed will be stable.

Thus, the role of solids (analogously to the role of liquid emulsifiers) in the formation of emulsions is two-fold: first, their presence in the two liquids hinders the break-up of one of them into droplets because of selective wetting conditions, as a result of which one or the other type of emulsion is formed; second, the stability of the emulsion obtained will depend on whether the given solid is capable of adhering to the surface of the droplets of the emulsion formed and forming a protective film there, which is necessary for stability; if such a film is formed, a stable emulsion is obtained, otherwise the emulsion is destroyed when mixing stops.

TABLE 9

Effect of Duration of Mixing on the Type of Emulsion Formed.

Oil phase	Aqueous phase	Glass				Plastic
		2 min.	20 min.	40 min.	60 min.	0.5 min.
Petroleum 1	Distilled water	o/w	o/w	w/o	w/o	w/o
Petroleum 1	Oil well water, 1	o/w	o/w	o/w	o/w	w/o
Petroleum 1	Oil well water, 2	o/w	o/w	o/w	w/o	w/o
Petroleum 2	Distilled water	o/w	o/w	o/w	w/o	w/o
Petroleum 2	Oil well water, 1	o/w	o/w	o/w	o/w	w/o
Petroleum 2	Oil well water, 2	o/w	o/w	o/w	o/w	w/o
Petroleum 3	Distilled water	o/w	o/w	w/o	w/o	w/o
Petroleum 3	Oil well water, 1	o/w	o/w	w/o	w/o	w/o
Petroleum 3	Oil well water, 2	o/w	o/w	o/w	w/o	w/o
Transformer oil	Distilled water	o/w	o/w	o/w	o/w	w/o
Transformer oil	Oil well water, 1	o/w	o/w	w/o	w/o	w/o
Transformer oil + 2% resins	Distilled water	o/w	o/w	w/o	w/o	w/o

TABLE 10

Effect of Addition of Kontakt to the Aqueous Phase on the Type of Emulsion Formed.

Oil phase	Aqueous phase	Iron	
		2 min.	60 min.
Petroleum 1	Oil well water, 1	w/o	w/o
Petroleum 2	Oil well water, 1	w/o	w/o
Petroleum 3	Oil well water, 1	w/o	w/o
Petroleum 1	Oil well water, 1, + 0.5% sodium sulfonates	o/w	o/w
Petroleum 2	Oil well water, 1, + 0.5% sodium sulfonates	o/w	o/w
Petroleum 3	Oil well water, 1, + 0.5% sodium sulfonates	o/w	o/w
Petroleum 1	Sodium sulfonates, 2%	o/w	o/w
Petroleum 2	Sodium sulfonates, 2%	o/w	o/w
Petroleum 3	Sodium sulfonates, 2%	o/w	o/w
Petroleum 1	Calcium sulfonates, 2%	o/w	w/o
Petroleum 2	Calcium sulfonates, 2%	o/w	w/o
Petroleum 3	Calcium sulfonates, 2%	o/w	w/o

TABLE 11

Effect of Selective Wetting on the Time Required to Change the Emulsion Type.

Oil phase	Aqueous phase	Time required for the formation of w/o emulsion, min.		
		glass	glass-plastic	plastic
Petroleum 1	Distilled water	43	8	0.5
Petroleum 1	Oil well water, 2	56	15	0.5
Petroleum 2	Distilled water	48	12	0.5
Petroleum 2	Oil well water, 2	x	8	0.5
Petroleum 3	Distilled water	25	8	0.5
Petroleum 3	Oil well water, 2	46	12	0.5
Transformer oil	Distilled water	x	18	0.5
Transformer oil	Oil well water, 2	37	14	0.5

Note. x — after 60 minutes the emulsion remained of the o/w type.

Effect of Duration of Mixing on the Type of Emulsion. Benkovsky and Zavorokhin [3] cast doubt on the views in our earlier papers concerning the effect of selective wetting on the type of emulsion formed. Their conclusions were based on data obtained in the formation of petroleum emulsions during prolonged stirring for 7 to 360 minutes.

In our studies of the effect of selective wetting on the type of emulsion, the liquids were usually mixed for 2 minutes, after which the emulsion type was determined. The object of the following experiments was to study the effect of duration of mixing on the type of emulsion formed. In these experiments the mixing was continued for different periods, from 30 seconds to 60 minutes, and in some cases even longer.

Experiments were carried out with mechanical mixing with the aid of a perforated plunger, at a speed used by the authors of the paper [3], 60 strokes/min.. In parallel experiments the same liquids were mixed by means of air. As usual, before each experiment the glass cylinder, plunger and tubes were kept in chromic mixture, and thoroughly washed and wetted with water. Water was first placed in the cylinder, followed by the oil. The iron and plastic cylinders, plungers, and tubes were washed with benzene before the experiments and dried in air. In these cylinders the oil was put in first, followed by water. The emulsion type was determined by pouring the emulsion out into a beaker of water.

In view of the fact that o/w emulsions are very unstable and separate out in 30-40 seconds after cessation of stirring, it is necessary to pour them into the beaker of water very quickly, otherwise they have time to settle before the emulsion type is determined*.

Three different petroleum and transformer oil were emulsified with distilled water and oil well water. The properties of the petroleum and waters are shown in Tables 5 and 6.

The results obtained in emulsification by the mechanical stirring method are shown in Table 7.

It follows from the data of Table 7 that when the liquids are mixed in a glass vessel even during one hour, the same o/w emulsion is formed as is obtained at the start of mixing. In iron and plastic cylinders stirring for 30 seconds is sufficient for the instant formation of w/o type emulsions.

The process of formation of the different types of emulsion is shown in Fig. 1 and 2; here transformer oil and distilled water were stirred with a glass or plastic plunger. The Photographs show clearly that when the glass plunger was used, the oil was broken up into droplets, while around the plastic plunger the water was enclosed within the oil with formation of w/o emulsion.

Fig. 3 shows a w/o emulsion of transformer oil and oil well water, obtained after 30 seconds' stirring in an iron cylinder and poured out into a beaker of water to determine its type.

The data shown in Table 7 are in full agreement with the results of our earlier studies on the effect of selective wetting on the type of emulsion.

In addition to emulsification of petroleum with oil well waters, they were also emulsified with solutions of sulfonates ("kontakt"). The results of the experiments are shown in Table 8, which shows that in presence of sulfonates in the aqueous phase, o/w emulsions are also formed in an iron cylinder, even after stirring for an hour**.

It was indicated earlier that "kontakt" has a high wetting power, and in this instance o/w instead of w/o emulsions are formed in its presence in the case of pure oil well waters. The o/w emulsions were unstable and were destroyed when stirring stopped.

Tables 9 and 10 show the data obtained in the emulsification of the same liquids, but when the mixing was done by means of air.

In the last two experiments (Tables 9 and 10), reversal of the emulsion phases took place in some cases after prolonged mixing. At the start of mixing, after 2 minutes (Table 9), o/w emulsion was obtained, and then phase reversal took place on continued stirring, and the result was a w/o emulsion.

The duration of mixing before formation of w/o emulsions varies, and depends on the properties of the oil and aqueous phases. Thus, the presence of 2% resins in transformer oil led to the formation of w/o emulsion in 38 minutes, while pure transformer oil did not give such an emulsion even after one hour.

For comparison, the same liquids were mixed in the same glass cylinder, but air was blown in through a plastic tube. In this case w/o type emulsions were formed at once for all liquids, 30-40 seconds after the start of mixing.

*It is not clear how the authors of the paper [3] were able to determine the emulsion type without cessation of stirring.

** See plate, page 308.

*** In a number of experiments the stirring was continued for 3 hours, and the emulsion type did not change.

The reversal of phases in the emulsions after prolonged stirring (in absence of an emulsifier which stabilizes the given type of emulsion) may be explained as follows. During prolonged stirring of the w/o emulsion first formed, gradual coalescence of the droplets of the disperse phase occurs. The coalescence process apparently commences not in the volume of the liquid, but at the surface of the walls and of the mixing tube. For this process to start it is necessary for the surface first to be wetted with the disperse phase, in this case oil, and for adhesion of separate droplets to it to take place.

The following experiments were carried out to confirm this view. The liquids were poured into a glass cylinder (as usual, thoroughly washed and wetted with water), and were mixed by air through a glass tube for 2 minutes. Emulsions of the o/w type were invariably obtained. Then, without cessation of mixing, a plastic tube was introduced into the cylinder, the glass tube was taken out, and the mixing continued by air blown through the plastic tube. Before it was introduced into the cylinder, this tube was wetted with the same oil as was being emulsified. The mixing continued till a w/o emulsion was formed.

A parallel experiment was performed with a plastic tube. On the introduction of the plastic tube the time needed for phase reversal was greatly shortened (Table 11).

These experiments confirm the supposition that coalescence of the drops of the disperse phase commences at the tube surface, and when this tube is more easily wetted by the oil, as when the plastic tube is introduced into o/w emulsion, phase reversal takes place more quickly.

A decrease of the mixing time is also found in the presence of resins. In the presence of resins transformer oil wets glass better, and therefore phase reversal takes place in 38 minutes, while pure oil does not give an emulsion of the w/o type even after mixing for an hour.

SUMMARY

1. The influence of selective wetting, not only on the type of emulsion, but also on phase reversal, was shown with examples of emulsions obtained by mixing transformer oil, kerosene, and petroleum with various aqueous solutions.

2. The following mechanism is proposed for phase reversal in emulsions. While the surface (tube, plunger) is well wetted by the aqueous phase, emulsion of the o/w type persists. When conditions arise which result in the wetting of this surface by oil, at first adhesion of the droplets of the disperse phase to the surface commences, and then these droplets begin to coalesce, which leads to the reversal of the emulsion type by simple enveloping of the dispersion medium between the coalescing droplets.

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* See Consultants Bureau Translation, page 15.

THE CHEMICAL NATURE OF ALGINIC ACIDS

I. ISOLATION OF FREE ALGINIC ACIDS

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Alginic acids are obtained from seaweeds, mainly from *Laminaria* and *Fucus*, by dissolving them out in aqueous alkaline solutions, for example, solutions of soda, potash, caustic alkali, ammonia, etc. Alginic acids are precipitated from alkaline solutions by strong acids or electrolytically. Voluminous, strongly hydrated colloidal precipitates are obtained. These precipitates were termed "algin" by Stanford [1]. After the discovery of the power of these precipitates to form salts, he termed them "alginic acid".

Precipitates of alginic acids, and particularly their water-soluble salts, the alginates, have found considerable practical application. The production of these substances is presently organized in nearly all countries with available supplies of seaweed. This has aroused considerable interest among chemists and biochemists in the chemical nature of alginic acids.

The development of views on the nature of alginic acids was mainly related to studies of their precipitates. Free alginic acids were not studied at all. As it is not possible within the limits of this paper to examine the history of the investigation of alginic acid precipitates, which forms the basis of modern views on its nature, we refer those interested to certain review articles [2, 3].

The modern views on the nature of alginic acid precipitates, which are usually identified with the concept of "alginic acid", are based on the following experimental data. Alginic acid precipitates which have been washed in water form strong films on drying, they do not melt or crystallize, they dissolve only in weak aqueous alkaline solutions, from which they can be recovered by acidifying with strong acids; they are partly soluble in concentrated alkalis and slightly soluble in water. Elementary analysis gives 44.39-39.00% carbon, and 5.47-4.60% hydrogen. Hydrolytic decomposition leads to the formation of mannuronic acid. The uronic acid content is in the range of 90-94%. During hydrolysis by hydrochloric acid, ~15% furfural and ~25% CO₂ is evolved [6]. The hydrolyzate yielded only compounds associated in origin with *D*-mannuronic acid. This led to the conclusion [6] that the fundamental structural unit in alginic acid precipitate is the mannuronic acid residue. Esterification introduced about two acid or alkyl groups per monomer unit. After methanolysis of the methylated precipitates, 2,3-dimethyl methyl mannuronide was isolated [13]. Oxidation of alginic acid precipitates gave mannosaccharic, oxalic, and dihydroxysuccinic acids. The pH of aqueous suspensions of the precipitates is ~3.5. In titration of the suspension with phenolphthalein, 1 g of the precipitates takes ~42 ml 0.1 N NaOH in direct titration, and ~56 ml in back titration [7]. Alginic acid precipitates react with alkalis, carbonates (in the cold), hydrates, amines, alkaloids, and other bases. Basic, complete and incomplete alginates may be formed. Alginates of polyvalent ions of the neutral salt type, and certain incomplete alginates of univalent ions are insoluble in water, and the others form viscous colloidal solutions. The molecular weight of sodium alginate, determined from the viscosity [5], was 15 thousand. The X-ray diagram of alginic acid precipitates resembles the X-ray diagram of cellulose [4].

The above experimental data provide a sufficient basis for the conclusion that alginic acid precipitates are high molecular compounds of an acid character, they have chain molecules composed of *D*-mannuronic acid residues, and the precipitates contain both combined and free carboxyl groups.

The generally accepted formulas for the precipitates of alginic acids (Figure 1) proposed by Nelson and Cretcher [6] and Dillon [8] generally agree with the above characterization of alginic acid precipitates, but they do not account for the considerable divergence of the titration results. Application of the solubility rule for alginates [9] to algin requires the presence in the latter of bound carboxyl groups.

Miwa [7], Barry and Dillon [10], and Lucas and Stewart [11] supposed that part of the carboxyl groups in alginic acid precipitates ("alginic acid", in their terminology) is bound in lactone form. This assumption is admissible on the basis of the formulas shown in Figure 1. In view of the low strength of ester linkages in polyuronic acids [12] and of the observed stability of the bound carboxyls to heat and action of acids (with and without heating), of the capacity of alginic acid precipitates to form ammonium salts only with concentrated ammonia, of the very low stability of the bound carboxyls even to weak alkalis, hydrates, carbonates, and even neutral salts of bi- and polyvalent cations,

and of the formation of 2,3-dimethyl methyl mannuronide on methanolysis [13], we consider that this assumption is unfounded. The above properties of the bound carboxyls in alginic acids are more in agreement with the view that they are bound in the form of acid anhydrides. We have, therefore, classified precipitates of alginic acids with polyanhydroacids [14] (Figure 2). At the same time we put forward the view that the formulas for polymannuronic acid, shown in Figure 1, should represent another substance, which differs from algin by being soluble in water and by having only free carboxyl groups.

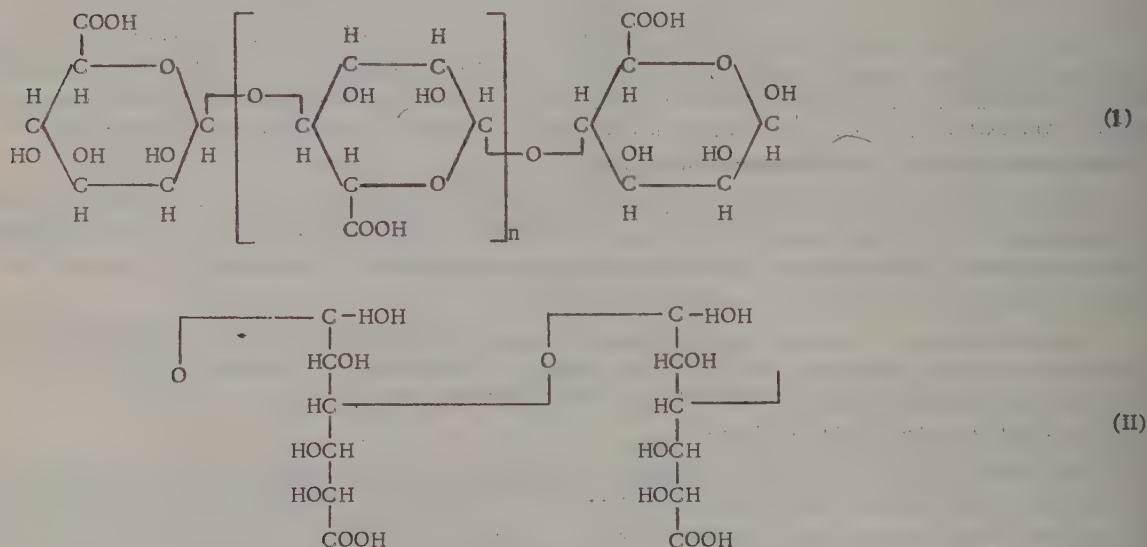


Figure 1. Theoretical formula for the structure of polymannuronic acid with cyclic monomer form, proposed by: I) Nelson and Cretcher for algin ("alginic acid" according to Nelson and Cretcher); II) by Dillon.

The aim of the present investigation was the development of methods for the isolation of free alginic acids. The following terms are used in the paper: "alginic acids" for the substances corresponding to the formula for polymannuronic acid (Figure 1, I or II), and "alginic acid precipitates", or "algin" (as equivalent terms) for the purified and washed precipitates of alginic acids obtained by the action of strong acids or harsh electrolysis conditions on alginates.

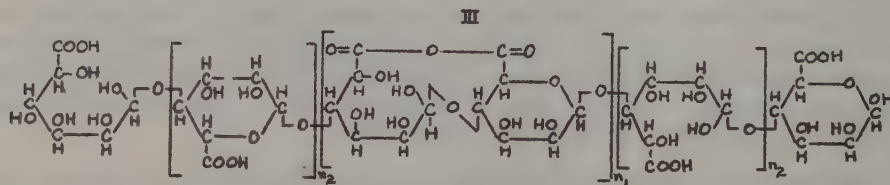


Figure 2. The author's proposed formula for the structure of algin.

EXPERIMENTAL

The starting material for the isolation of alginic acids was sodium alginate obtained from White Sea Laminaria by the usual technique. The sodium alginate had the following characteristics: moisture 15.31%, ash 27.21%, viscosity of 1% aqueous solution 4.61° E, alginic acid content 79.73%.

Method of isolation. It is well known that only strong acids are capable of isolating alginic acid precipitates from solutions of alginates; weak acids in low concentration do not precipitate alginic acids. From this fact and the supposed solubility of alginic acids we concluded that when solutions of alginate and a weak acid are mixed, the weak acid reacts with the alginate and liberates alginic acids, but conditions are not created for the interaction of the carboxyl groups of the alginic acids. All the carboxyl groups remain free, and, therefore, the alginic acids remain

in solution. If the salt of the weak acid and the excess of weak acid are removed from the solution by dialysis, only alginic acids should remain in solution. The solutions were dialyzed in a dialyzer of the usual type, with a vessel capacity of 400 ml.

For the isolation of alginic acids, 2 g of the alginate was dissolved in 200 ml water, and 200 ml of 10% acetic acid solution was slowly added to the solution with stirring. The homogeneous solution obtained was filtered through a No. 1 glass filter and then dialyzed till the dialyzate was neutral to litmus. The duration of the dialysis was 8-10 days; after that ~ 200 ml of the solution was removed from the dialyzer and replaced by the same volume of a 10% solution of acetic acid. The solution was subjected to repeated dialysis. Thus, the alginate solution was treated with acid three times. As a result of such treatment, a homogeneous, colorless, opalescent solution was obtained each time. The residual acetic acid was driven off in a vacuum until a distillate neutral to litmus was obtained. In no instance was precipitation of alginic acid observed. After removal of the acid, the solution was brought up to the original concentration with distilled water and investigated. Similar results were obtained by the treatment of alginate solutions with weaker solutions of formic and sulfurous acids.

Analytical data for alginic acid solutions (Table 1) show that, in their ash content, the alginic acids obtained are comparable with the best specimens of alginic acid precipitates studied to date.

Alkali Titration of Alginic Acids. The titration was carried out by the usual methods. The titration results are shown in Table 2 and Fig. 3.

TABLE 1
Change in the Concentration and Ash Content of Alginic Acid Solutions in their Isolation from Sodium Alginate Solution. (Weight of Sodium Alginate Sample was 2 g)

Sequence number of acetic acid treatments	Concentration of solution, %	Obtained after dialysis, in g	Solution concentration, %	Ash, %
0	—	—	—	27.73
1	1	1.836	0.459	3.816
2	0.459	1.056	0.264	1.984
3	0.264	0.460	0.108	0.261

Total yield 1.727 g, or 86.4%.

TABLE 2
Results of Titration of Alginic Acids

Method of titration	Acid solution taken, g	Concentration, %	Alginic acids, g	0.1 N NaOH taken, ml	Neutralization equivalent
Direct	50	0.311	0.1555	8.75	177.5
Reverse	50	0.311	0.1555	8.85	175.7
Potentiometric . .	50	0.311	0.1555	8.85	175.7
Conductimetric . .	37.75	0.320	0.1208	6.75	179.9

The titration results showed no difference between the amounts of alkali used in direct and back titration of solutions of alginic acids, and an absence, on the potentiometric and conductimetric titration curves, of any inflexions which are not due to the titration of solutions of pure free acids.

On acidification of solutions of alginic acids with solutions of strong acids (HCl , H_2SO_4), a flocculent precipitate is gradually formed and deposited. The precipitate dissolved in alkalis. From the alkaline solutions strong acids again gave a precipitate, also soluble in alkalis. The elementary analysis of the precipitate in % was: C — 39.93, H — 4.54. The elementary composition calculated from the formula for the structure $(\text{C}_6\text{H}_8\text{O}_6)_n$: C — 40.9% and H — 4.54%. Thus, the properties and composition of the precipitate correspond to the properties and composition of algin.

Viscosity of 0.1% Solution of Alginic Acids. 0.1% Solution of alginic acids was prepared by dilution of the solution of alginic acids obtained after dialysis. The solution had pH 2.34. The viscosity was determined in a thermostatically controlled Ostwald viscosimeter, with an average efflux time of 75.4 seconds at 20°, at increasing and decreasing temperatures for the same solution. The results of the determinations are shown in Fig. 4. For comparison, Fig. 4 also shows the viscosity changes, in the same conditions, of 0.1% solution of sodium alginate, prepared by

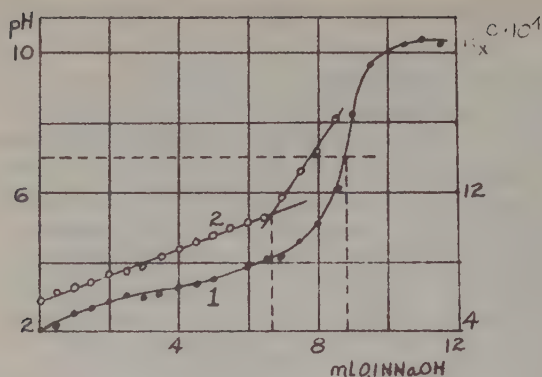


Fig. 3. Potentiometric (1) and conductimetric (2) titration of solutions of alginic acids.

ments showed that even on moderate heating of solutions of alginic acids considerable irreversible changes of viscosity take place, which does not occur when alginate solutions are heated. The molecular weight of the alginic acids, determined from the viscosity [5], was 221 thousand, and that of sodium alginate was 110 thousand (in the calculation the value $K = 1.5 \cdot 10^{-3}$ was taken).

Composition and Properties of Sodium Alginates Obtained by Neutralization of a Solution of Alginic Acids

To prepare sodium alginates, solutions of alginic acids were neutralized by 0.1 N NaOH, the alkali being added in varying amounts up to the formation of the complete alginate. If no precipitate was formed as the result of mixing the alkali solution and the solution of alginic acids, the products formed were considered to be soluble in water. The properties of the alginates obtained are shown in Table 3.

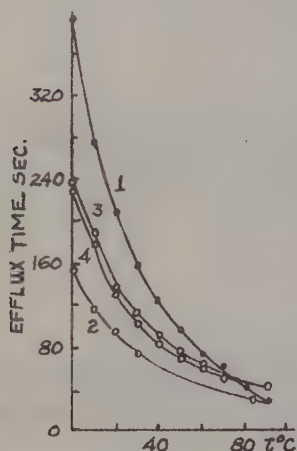


Fig. 4. Change of viscosity of 0.1% solution of alginic acids: 1) on heating; 2) on cooling; the same, for sodium alginate; 3) on heating; 4) on cooling.

Composition and Solubility of Alginates of Calcium and Barium. Two methods were used for the preparation of calcium and barium alginates; 1) the addition to solutions of alginic acids of solutions of salts

TABLE 3
Solubility of Sodium Alginates Obtained by Neutralization of Solutions of Alginic Acids

Alkali added, in parts of neutralization equivalent	Ash content of alginate, %	Sodium content, %	Solubility in water
0.1	2.97	0.97	Complete
0.4	9.05	4.02	Complete
0.8	18.02	9.83	Complete
1.0	26.32	11.35	Complete
1.1	26.81	11.82	Complete

neutralization of alginic acid by 0.1 N NaOH and purified by precipitation and washing with alcohol. The ash content of the alginate was 24.45%, the pH of the alginate solution was 7.4. The results of the experi-

The results of the experiments show that all incomplete sodium alginates obtained from solutions of alginic acids are completely soluble in water; they differ in this respect from the incomplete alginates obtained from precipitates of alginic acids [11].

TABLE 4
Composition and Properties of Alginates of Calcium and Barium, Obtained from Solutions of Alginic Acids

Reagent	Amount of cation added, in % of the theoretically required to form alginate		Cation content found, %	Solubility in water
	Neutral salt type	Basic or mixed salt type		
CaCl_2	40	20	9.82	Insoluble
CaCl_2	100	50	9.93	Insoluble
$\text{Ca}(\text{CH}_3\text{COO})_2$..	100	50	8.79	Insoluble
$\text{Ca}(\text{CH}_3\text{COO})_2$..	200	100	9.05	Insoluble
$\text{Ca}(\text{OH})_2$	40	20	3.02	Complete
$\text{Ca}(\text{OH})_2$	100	50	9.05	Complete
$\text{Ca}(\text{OH})_2^*$	150	75	13.91	Complete
$\text{Ca}(\text{OH})_2$	200	100**	10.43	Insoluble
$\text{Ca}(\text{OH})_2$	200	100***	15.84	Complete
$\text{Ba}(\text{OH})_2$	150	75	32.17	Complete

* The molecular weight of calcium alginate, determined from the viscosity with the value $K = 1.5 \cdot 10^{-3}$ [5], was 53 thousand.

** precipitate

*** solution

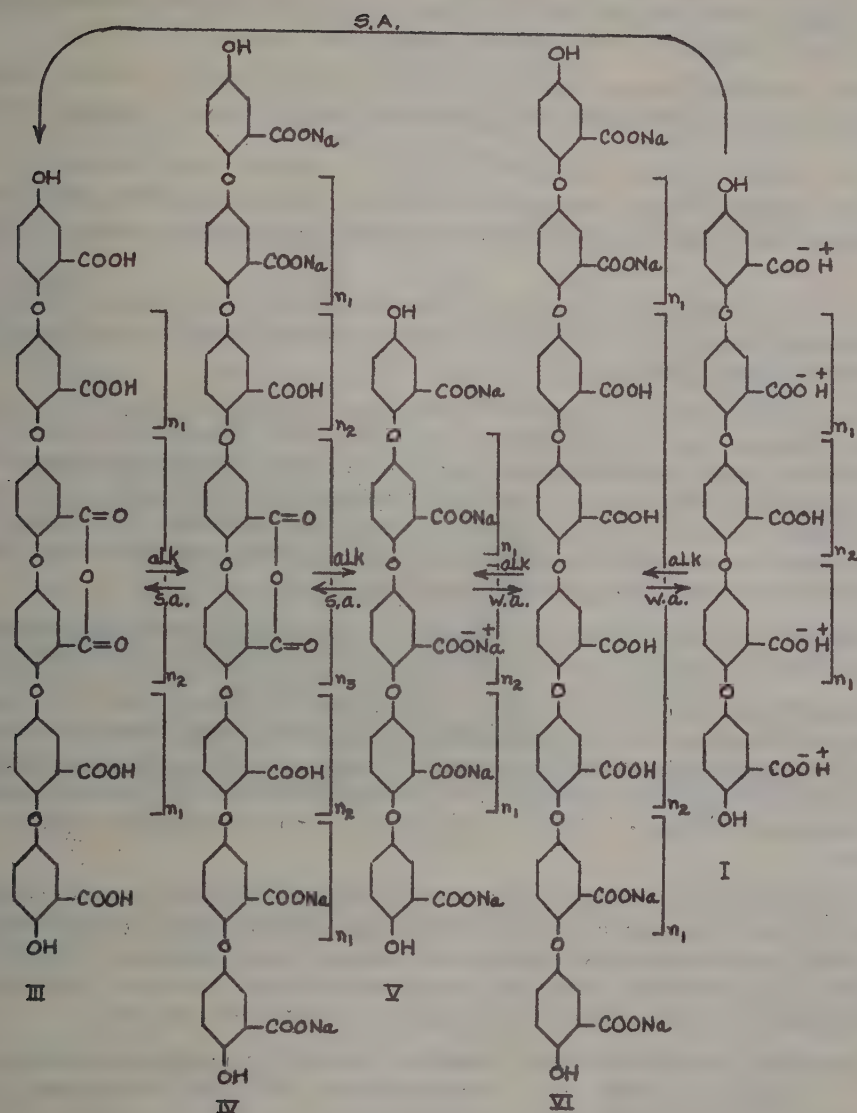


Fig. 5. Scheme of interconversions: algin (III) \rightarrow incomplete alginate (IV) \rightarrow complete alginate (V) \rightarrow incomplete alginate from alginic acids (VI) \rightarrow alginic acid (I) (s.a. - action of strong acids, w.a. - action of weak acids).

of calcium or barium with a cation content of $\sim 2-3$ g/l; 2) neutralization of solutions of alginic acids by solutions of calcium or barium hydroxides. In the first case precipitates of calcium or barium alginates were always obtained, and in the second case the precipitates were formed only in a strongly alkaline medium. The properties of the alginates obtained are shown in Table 4.

The results of the experiments show that neutralization of solutions of alginic acids by calcium or barium hydroxides gave water-soluble alginates of calcium and barium, and the cation content of some of the soluble alginates greatly exceeded the cation content in alginates of the neutral salt type.

Preparation of Alginic Acid Esters. Esters were prepared by the same technique that was used for the alginic acids themselves, but with the use of electrodialysis (1.5 V/cm). After purification of the esters to remove salts and excess acetic acid the dialyzer contained a homogeneous strongly opalescent colloidal solution, strongly resembling a solution of alginic acids. Analysis of the solution gave acetyl group contents of 30.60 and 30.06%. Calculation of the acetyl group content gives 19.7% for the monoacetate and 33.08% for the diacetate.

The analytical results show that acetic esters close to diacetates were obtained. The esters obtained were completely soluble in water, so differing from the analogous esters obtained from precipitates of alginic acids.

DISCUSSION

By the action of solutions of strong acids on alginate solutions the liberated alginic acids are precipitated. Up to the present time these precipitates were assumed to be "alginic acids" with the structural formulas shown in Fig. 1.

The data in the experimental section of this paper show that as the result of treatment of aqueous solutions of alginates with aqueous solutions of weak acids taken in considerable excess, alginic acids are again liberated, but are not precipitated, remaining in solution.

Alginic acids obtained in the form of aqueous solutions differ from algin; they are soluble in water, and contain only free carboxyl groups; they form precipitates of alginic acids by the action of strong acids; on neutralization they form only water-soluble incomplete sodium alginates; they form only water-soluble acetyl esters; neutralization of solutions of alginic acids with calcium or barium hydroxides gives water-soluble alginates of calcium or barium. Up to the present time these alginates could not be obtained in a soluble form from precipitates of alginic acids and were considered to be typical insoluble alginates. However, all alginates of the neutral salt type are exactly the same, both for the precipitates and the solutions of alginic acids.

The above properties of solutions of alginic acids, in comparison with the corresponding properties of precipitates of alginic acids, show that this is a case of two substances different in the physico-chemical sense.

In their composition and properties free alginic acids correspond to the formula for polymannuronic acid, and are therefore quite definite substances in the chemical sense. Precipitates of alginic acids are obtained from free alginic acids, and are therefore derivatives of the latter. They contain both bound and free carboxyl groups. The ratio of these depends on the preparation conditions. The preparation conditions also determine the physico-chemical properties. Therefore, precipitates of alginic acids have neither constant composition nor constant physico-chemical properties.

In view of this we propose to attribute the concept of "alginic acid" and the structural formula for alginic acid (polymannuronic acid, Fig. 1) to the newly-prepared substance, and to ascribe a new structural formula to precipitates of alginic acids, which would describe their properties more correctly. In our present state of knowledge the most complete description of the properties of alginic acid precipitates is given by the formula for the incomplete acid anhydride of polymannuronic acid. Fuller details will be given in a separate communication.

From the data in the experimental section it can be concluded that we achieved the following interconversion cycle: algin \rightarrow incomplete alginate \rightarrow complete alginate \rightarrow incomplete alginate \rightarrow free alginic acids \rightarrow algin. This cycle is diagrammatically shown in the structural formulas in Fig. 5. Attention is drawn to the difference between the structure of alginic acids I, algin III, and incomplete alginates IV and VI.

Alginic acids are unstable in the free state. Evidence for this is the sharp decrease of molecular weight on conversion to alginates, irreversible changes of viscosity on relatively moderate heating in conditions in which sodium alginate remains practically unchanged in viscosity, and their ease of transition into algin and alginates. The stability of precipitates of alginic acids to heat and the action of acids is well known.

SUMMARY

1. By treatment of alginate solutions with solutions of weak acids, water-soluble alginic acids without bound carboxyl groups were isolated.
2. In their physico-chemical properties and in the properties of some of their derivatives, the alginic acids differ from precipitates of alginic acids, or algin.
3. Different water-soluble alginates of calcium and barium were prepared by neutralization of solutions of alginic acids with solutions of calcium or barium hydroxides.
4. Free alginic acids are unstable and readily pass into algin or alginates.

5. The following interconversion cycle was achieved: algin \rightarrow incomplete alginate \rightarrow complete alginate \rightarrow incomplete alginate \rightarrow alginic acids \rightarrow algin.

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GELATION OF FRESHLY PREPARED SOLS OF VANADIUM PENTOXIDE

I. F. Efremov

In papers published in recent years on electron-microscopic and electronographic investigations of V_2O_5 sols [1, 2] it is shown that the particles in the sol change into short rods from practically isodiametric lumps in the course of several days after preparation. According to the data of Bromberg and others [2], for a sol two days old the maximum on the particle length distribution curve corresponds to approximately 0.1μ , and for a sol 5 days old, $\sim 0.4 \mu$.

As the gel forming capacity of such sols is usually thought to be associated with the presence of very long particles, it was of interest to verify the possibility of gelation in freshly prepared sols.

It is noted in a number of papers on the coagulation of V_2O_5 sols that sols 2-3 days old gelate under the action of electrolytes only when their concentration is relatively high [3].

Rabinerson [4] in his studies used V_2O_5 sols more than one month old, but we found no indications in his paper of the behavior of freshly prepared sols. We therefore prepared V_2O_5 sol from ammonium vanadate by the usual method. The V_2O_5 precipitate was washed with water, transferred from the filter into a flask, an appropriate volume of water was added, and the sol was left for 1 hour for peptization, after which gelation experiments were carried out on the non-dialyzed sol. The viscosity of the sol obtained was 5% higher than the viscosity of water and remained practically unchanged for 5 days. The V_2O_5 concentration in the sol was 2.34 g/liter.

For gelation, 0.25 ml of NaCl solution of a concentration of 200 mg equiv. per liter, was added to 1 ml of the sol in a test tube of 15 mm diameter. On the next day, 16 hours after preparation of the sol, all 5 specimens formed weak gels which did not withstand inversion of the test tube. Shaking of the gels in the test tubes resulted in the formation of separate clots, as a result of which the gels became opaque and a layer of liquid appeared on top. Subsequently, syneresis took place very slowly, but the strength both of the shaken and the undisturbed gels remained inadequate.

After these experiments there need be no doubt concerning the capacity of freshly prepared V_2O_5 sols for gelation. The gels obtained by Rabinerson from aged sols also did not have high strength, and therefore he was obliged to prepare them in narrow tubes (7 mm) but nevertheless they still slowly flowed down when these tubes were inverted.

The following experiments were carried out with the aim of finding gelation conditions which would permit sufficiently rapid gelation of sols of low concentration. It was found that a one-day-old sol gelled on the following day after the addition of 1:1 solution of NaCl of a concentration of 50 mg equiv./liter. The addition of 1-2 drops of 0.01 N NaOH solution to 1 ml of the sol shortened the gelation time and sharply increased the strength of the gels, which could no longer be poured out of the tubes.

On the assumption that the hydrate layers which stabilize the sol particles may be gradually destroyed by approach of the latter, and that this process may be accelerated by the action of dehydrating agents [5], we decided to accelerate gelation by addition of acetone. The problem was solved by this method, and gels containing very small amounts (less than 0.1% by weight) of V_2O_5 could be prepared.

The experiments were carried out as follows: 1 ml acetone and 1-2 drops of 0.01 N NaOH solution were added to 1 ml of a three-day-old sol. The solution was stirred, 1 ml of NaCl solution of the concentration given above was rapidly added, and the mixture was shaken vigorously. A firm gel, which could not be poured out of a wide test tube, was formed at the instant of shaking. The gelation time was a fraction of a second. At very low sol concentrations (of the order of less than 0.05%) the gelation time is measured in minutes and tens of minutes.

Subsequently, gelation of four and five-day-old sols of not-too-low a concentration was effected by the addition of acetone alone, although the time required in this case was greater. Trial experiments with methyl alcohol showed that it has the same effect as acetone.

Discussion of the results of these experiments leads to the following conclusions:

1. The presence of very long particles of the disperse phase (of the order of several μ), which appear in aged V_2O_5 sols, is not essential for gelation. Sols 1-2 days old which were gelated in our experiments, according to the electronographic studies cited above, have particles of length not greater than 0.1-0.3 μ .

2. The relatively low concentration of the freshly prepared sols ($\sim 0.1\%$ and less) which gelate practically instantaneously, excludes the possibility of formation of a skeleton network from sol particles in direct contact with each other.

3. Addition of electrolytes is not essential for gelation.

4. The time of gelation is primarily determined by the kinetics of rearrangement of the hydrate coatings by the action of destabilizing factors.

In our view, the gelation process in V_2O_5 sols is due to the interaction of the sol particles at considerable distances. It is known that the forces of attraction can prevail over the forces of repulsion not only when the distances between colloidal particles are small, which leads to coagulation, but also when they are large, when the energy barrier separating the particles is retained [6]. This situation is reached for a relatively large radius of action of the van der Waals forces and not very great changes in the ionic and hydrate coatings. In fact, in our sols gelation commenced when the sol particles were separated by distances of the order of their own dimensions, that is, 1000-2000 Å. Preliminary treatment by acetone diminishes the "splitting pressure" of the hydrate, and partly of the ionic layers. However, at low electrolyte concentrations in the sol, the latter still have a sufficiently wide radius of action, which is rapidly decreased by the addition of further ions.

There can hardly be any doubt that in the time required for adding acetone and the electrolyte, totalling 2-3 seconds, condensation of the primary particles to aggregates of enormous length cannot take place. Moreover, the role of long particles in general seems to us to be greatly exaggerated. If the presence of very long particles only was sufficient to cause gelation, the question arises why sols several years old, especially sols of not-very-low concentration, do not gelate spontaneously.

We consider the role of very long particles to consist mainly in increasing the shear strength of the gel, in comparison with the shear strength in absence of a continuous network of particles. However, this secondary factor has no direct relation to the causes of gelation. It should be noted that the decrease of fluidity of gelatable solutions is affected relatively little by the presence of long, intertwined particles. We need only mention the figures shown in Rabinerson's papers, from which it is seen that even gels obtained from old V_2O_5 sols in a narrow inverted test tube do not flow down very slowly.

SUMMARY

1. A description of gelation experiments with freshly prepared vanadium pentoxide sols is given.

2. Discussion of the results of the work leads to the conclusion that the gelation of these sols occurs as the result of interaction of colloidal particles at great distances, in accordance with the theory of particle interaction developed by B. V. Deryagin.

In conclusion, I express my gratitude to Associate Member B. V. Deryagin of the Academy of Sciences, USSR, for his interest in this research.

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CHANGE OF THE FINE STRUCTURE OF COLLAGEN ON SWELLING IN WATER VAPOR

A. L. Zaides

Collagen, the fibrous protein of the corium of the skin covering, belongs to high molecular compounds capable of considerable absorption of moisture. Naturally, therefore, a large number of papers are devoted to studies of this question [1]. However, to the present time there are no data on changes in the fine structure of collagen in relation to the amount of moisture absorbed by the collagen or to the vapor pressure of the medium.

The object of the present investigation was the study of changes in the fine structure of collagen for various pressures of vapor in the surrounding medium.

The X-ray method of structural analysis was used for the investigation. The X-ray photographs were taken with a BSV-60 tube with filtered copper radiation at a voltage of 30 kV and current strength of 22 mA. The time of exposure was about 15 hours.

The specimens for the diagrams were prepared as follows: bundles of the raw fibers, taken from the frontal part of raw hides, were placed in thin-walled glass capillaries (the capillary walls must be capable of flexing under finger pressure), the lower ends of which under the fibers contained saturated salt solutions with the corresponding vapor pressures. The capillaries were then sealed and held for several months at room temperature before the X-ray photographs were taken. The compounds giving constant vapor pressure used were: strong sulfuric acid (water vapor pressure φ was taken equal to 0), saturated salt solutions - zinc chloride ($\varphi = 10\%$), lithium chloride ($\varphi = 15\%$), potassium carbonate ($\varphi = 43\%$), potassium nitrate ($\varphi = 45\%$), calcium nitrate ($\varphi = 56\%$), sodium nitrate ($\varphi = 66\%$), oxalic acid ($\varphi = 76\%$), sodium sulfate ($\varphi = 93\%$), disodium hydrogen phosphate ($\varphi = 95\%$), and water ($\varphi = 100\%$).

For a more accurate determination of the interplane spacings, the photographs were taken with a standard. Metallic silver powder was used for this. The interplane distances were determined with the aid of the Bragg's - Vulf Equation:

$$\lambda = 2d \sin \frac{\theta}{2} ,$$

The X-ray diagram of collagen shows a series of interference rings or half-arcs (if the specimen is oriented), of which the most characteristic are: an interference ring corresponding to a distance of 2.9 Å, which characterizes the repeat of amino-acids along the length of the collagen chain, and rings corresponding to distances of 4.5 and ~ 11 Å, which characterize the mutual arrangement of the chains: the first corresponds to the distance between principal chains in contact, and the second, the distance between the chains in the direction of the side chains.

When collagen is humidified, mainly the distance between the side chains is changed [2]. Therefore, the present study deals only with the interplane spacings which correspond to the disposition of the side chains (~ 11 Å).

The results obtained (Table 1) show that at 76% relative humidity of the medium there is a jump in the value of the interplane spacings between the side chains (Fig. 1). At higher values of relative humidity the X-ray diagram no longer changes: the interplane spacings remain constant within the limits of experimental error. At lower values of relative humidity of the medium, there is a relatively small gradual increase in the values of the interplane spacings.

The existence of a jump in the values of the interplane spacings with variations of vapor pressure indicates a difference in the nature of attachment of the first amounts of water at low vapor pressures in the medium, and the water bound at 76% relative humidity and higher.

Binding of water with a thermal effect should occur at active groups. Such hydration centers in collagen may be peptide linkages, and hydroxyl, carboxyl, and amino groups.

TABLE 1

Change of the Spacing Between Planes in the Direction of the Disposition of the Side Chains in Relation to the Relative Vapor Pressure of the Medium (φ)

Compound used for humidifying the medium	φ , in %	d, in Å	Compound used for humidifying the medium	φ , in %	d, in Å
H ₂ SO ₄	0	11.0	NaNO ₂	66	12.1
ZnCl ₂	10	10.7	H ₂ C ₂ O ₄ · 2H ₂ O	76	14.1
LiCl	15	11.2	Na ₂ SO ₄	93	14.2
K ₂ CO ₃	43	11.2	Na ₂ HPO ₄	95	14.2
KNO ₃	45	11.7	H ₂ O	100	14.4
Ca(NO ₃) ₂	56	11.9			

If it is assumed that one molecule of water becomes attached to each active group, then, as is indicated by Mikhailov [3], the peptide linkages should be attached to 19.1 g, the hydroxyl groups to 8.2 g, the carboxyl groups to 8.9 g, and the basic groups to 1.8 g water per 100 g protein.

The question as to which groups in the protein are hydrated first may be solved by the method of X-ray structure analysis. For this, however, it is necessary to have data on the amount of water bound by collagen in relation to the vapor pressure of the medium. No such data exist for fibers. Most of the investigations are devoted to studies of sorption of water by connective tissue, rawhide, powder prepared from it, or finished leather. Different authors obtained different amounts of bound water at 100% saturation of the surrounding air; the value apparently depends on the degree of subdivision of the collagen (powder or pieces) and on the preliminary treatment (drying by alcohol and ether, or in air). However, the nature of the curve for water sorption in the first stages (up to 80-90% relative humidity) does not depend on the above treatments.

Fig. 2 shows the results obtained by Sokolov, Dulitskaya, Zaides, and Kolyakova [4] for rawhide powder, and by Bull [5] for pieces of collagen thoroughly purified by dialysis. The curves obtained by these authors coincide. This agreement between the results justifies our application of the data on bound water to separate fibers placed in a medium of definite vapor density.

As was already indicated earlier, the jump in the values of the interplane spacings in the direction of disposition of the side chains is observed at approximately 76% relative humidity. At this humidity, as Fig. 2 shows, about 27 g water is absorbed by 100 g protein. This value corresponds to hydration of the peptide linkages and hydroxyl groups ($19.1 + 8.2 = 27.3$). In subsequent absorption, the water is bound along the line of the side chains; this results in an increase of the distance between the side chains up to ~ 14 Å. Change of distance from ~ 11 to ~ 14 Å between the side chains indicates that only one molecule of water can become attached in this direction.

The results show that the first amounts of water, bound with the greatest thermal effect, hydrate the peptide and possibly also the hydroxyl groups. Hydration of the active groups in the side chains begins only after these groups are saturated with water.

Entry of the first amounts of water into the collagen cell without significant alteration of the dimensions of the latter is possible only if the amount of space in the cell is sufficiently great to accommodate

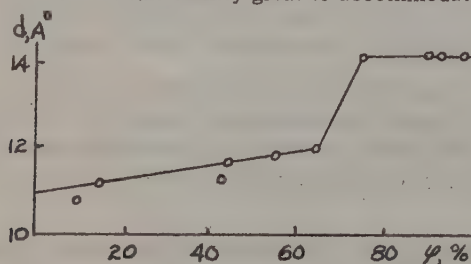


Fig. 1. Changes of the distance between the side chains of collagen with the vapor pressure of the medium.

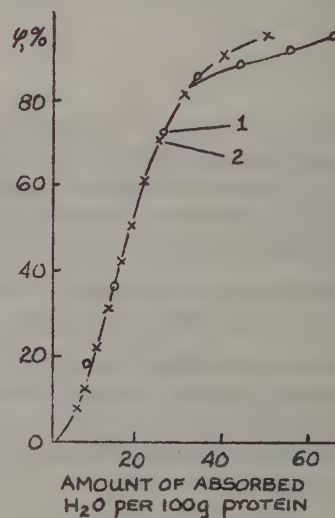


Fig. 2. Variation of the amount of water absorbed by collagen with vapor pressure of the medium: 1) results of Sokolov et al [4]; 2) Bull's data.

a water molecule. Natural crystals are usually built up on the dense packing principle. However, this principle is not always obeyed for proteins. Thus, Kroifut [6] found, in a study of protein crystals isolated from globular proteins, that protein crystals are permeable to water, to ions, and even to such relatively large molecules as organic dyes.

In examination of the X-ray diagrams of collagen at various vapor pressures it is seen that the interference spots corresponding to the disposition of the side chains decrease in length. Up to 15% relative humidity of the medium, the spots are generally weak and indistinct. Sharper X-ray diagrams are obtained at a relative humidity of 45%. However, the length of the interference maxima gradually decreases. The decrease in the length of the spots is due to increase in the degree of orientation.

The degree of orientation may be determined from measurements of half-widths of the microphotometric curves, from the Equation:

$$H = \frac{90 - h}{90} \cdot 100,$$

where h is the half-width angle of the interference spot, and H is the degree of orientation.

A special attachment to the automatically recording microphotometer was constructed for arc photometry.

The dependence of the degree of orientation of the interference spots corresponding to the positions of the side chains, on the relative vapor pressure of the medium, is given by the following data:

Relative Vapor Pressure in the Medium, %	0	15	43	56	66	76	93	95	100
Degree of Orientation, H, %	64	63	69	70,5	72	74,5	78	80	73

With the exception of the values of 0 and 100% relative vapor pressure, there is a gradual increase of the degree of orientation with increase of water content in the collagen.

The values obtained for $\varphi = 0$ are inconclusive, as the amount of sulfuric acid in the capillaries is very small (1-2 drops) and the small amounts of moisture in the air-dry fibers may dilute the sulfuric acid; as a result the pressure of water vapor may be higher. With regard to 100% relative humidity the supposition may be made that at this degree of humidity the excess of water in the fibers is so great as to act in a disorienting direction. According to the data in the paper of Sokolov, Dulitskaya, Zaides, and Kolyakova [4], at 96% relative humidity, raw-hide powder absorbs 64.9% water, and at 100% relative humidity, 103.4%. This sharp increase in the moisture content may produce disorientation of the side chains.

The question of orientation on humidification may be approached on the basis of purely thermodynamical calculations. It is true that such calculations are arbitrary, as thermodynamics deals only with equilibrium systems. It is difficult to say at the present time whether the interaction of dry collagen with water reaches an equilibrium state, as the drying curve does not coincide with the humidification curve (there is a hysteresis loop). However, since the results of thermodynamical calculations are confirmed by X-ray data, we consider that they may be quoted. The thermodynamical calculations relate to the orientation of water in collagen. In this instance it is not free water that is considered, but water bound in the system, where orientation of one components leads to orientation of the other. Therefore, orientation of the water molecules indicates an ordered state of the whole system.

The experimental data used in the calculations are taken from the papers by Sokolov *et al* [4] and Bull [5].

A measure of affinity between substances is the change in the free energy of formation of a system. The change of free energy in an isothermal process may be expressed by the Equation:

$$\Delta F = \Delta H + T \Delta S,$$

where F is the free energy; H is the heat content; S is the entropy; and T is the absolute temperature.

The magnitude and change of the entropy term in the process of humidification of collagen may serve as a measure of the increase or decrease of the degree of orientation. If the entropy term in the Equation increases, this indicates a decreasing degree of orientation; if the entropy term decreases, the degree of orientation should increase. The values of ΔF and ΔH may be determined from experimental data.

The change in the free energy of a system is determined by the Equation:

$$\Delta F = RT \ln \frac{p}{p_0}.$$

TABLE 2

Change of Free Energy, Heat Content, and Entropy During Sorption of Water by Collagen.

Relative humidity, %	Water absorption, in g/100 g of absolutely dry substance	ΔH , cal/mole	ΔF , cal/mole	$\Delta H - \Delta F$	ΔS cal/mole deg.
4	5	2480	1800	680	2.28
20	10	1760	950	810	2.38
40	15	1160	540	600	2.10
57	20	800	350	450	1.57
70	25	680	210	470	1.58
79	30	500	131	369	1.24
89	40	320	70	250	0.84

where R is the gas constant; T is the absolute temperature; p and p_0 are the pressures of water vapor over the substance and water at the given temperature; ΔF was calculated from Bull's data.

The change of heat content was determined from the differential heats of swelling of collagen in water. This value was found from the heats of adsorption of water given in the paper [4]. The results obtained are shown in Table 2.

It is seen from Table 2 that the entropy of the system decreases with humidification, which indicates an increase of the degree of orientation.

As was already indicated above, at low humidity values there is a small increase in the interplane spacings in the direction of the side chains (from 11 to 12.1 Å). This fact, and also the increase in the degree of orientation of the side chains with increase in the relative humidity of the medium leads us to the supposition that in the dry state the side chains of collagen are in a deformed, somewhat stressed condition. This supposition is supported by the fact that absolutely dry collagen gives a disoriented X-ray diagram. As the collagen is humidified, the chains gradually straighten (removal of stress). The side chains reach the greatest degree of orientation when their effect on each other is completely weakened by the water molecule separating them.

SUMMARY

1. The first molecules of water, which are bound by collagen with the greatest thermal effect, do not affect the X-ray diagram of collagen significantly. This is evidence that the first amounts of water combine with the peptide and hydroxyl groups.

2. At a relative humidity of the air of 76% and higher one molecule of water is incorporated in the direction of the disposition of the side chains. This incorporation leads to an increase of the interplane spacing in this direction of up to ~ 14 Å.

3. The degree of orientation of the side chains increases with increase in the amount of sorbed water. On the basis of this fact it may be considered that in dry specimens the side chains are in a deformed state. As the collagen is humidified the chains straighten, and the straightening reaches its maximum value when the mutual effect of the charged centers of the side chains is weakened by the incorporation of a water molecule between them. The fact that the chains become oriented during humidification is confirmed by theoretical calculations.

In conclusion, I express my gratitude to A. N. Mikhailov for valuable advice.

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INVESTIGATION OF THE STRUCTURE OF SYNTHETIC POLYAMIDES

V. THERMOGRAPHIC DATA ON STRUCTURAL TRANSFORMATIONS IN SYNTHETIC POLYAMIDES

N. V. Mikhailov and V. O. Klesman

Up to 1947-1949, thermographic analysis was used mainly for investigating minerals and metals [1] and was hardly ever applied to studies of structural and chemical transformations which may take place when high polymers are heated or cooled. We know of the existence of papers on the thermography of polymers in the case of polyamides, polyurethanes, cellulose, polyethylenes, and some other high polymers [2]. The results of thermographic investigations are usually presented in the form of heating or cooling curves for the substance in temperature-time coordinates. In most cases the authors of the papers cited above used this relatively simple method for recording the curves to prove a first order phase transition in the melting or solidification of the polymer. In the USSR wide acceptance has been gained by the method of registration of thermographic curves with the aid of differential automatic recording, proposed by Kurnakov [1, 3].

The scheme of Kurnakov's pyrometer is shown in Fig. 1,* where 1 is the drum on which the photosensitive paper is attached; 2 are mirror galvanometers; the circuit of one contains a simple thermocouple for recording temperature-time curves, and of the other, a differential thermocouple for recording time-temperature difference curves; 3 are light sources; 4 is a heater; 5 is a rheostat; 6 is a compound thermocouple.

In the thermographic method, the test substance and the standard are placed in a refractory crucible. In view of a number of peculiarities of our samples, we used ordinary test tubes of high melting glass, which were selected to be as low in weight and as much alike in weight, as possible, and of a shape convenient for filling with the specimens. About 1-1.5 g amounts of the finely-divided substance and standard were placed in the tubes, which were then fitted with round ceramic plates with a hole in the center and slits in the sides. The hole in the center of the plate made it possible to arrange the thermocouple in the specimen or standard. Copper-constantan thermocouples were used in all experiments. The simple thermocouples were calibrated by melting and transition points of chemically pure substances (naphthalene, tin, bismuth, *p*-dichlorobenzene, potassium thiocyanate, ammonium nitrate).

The aim of the present work was to apply the thermographic method to investigation of structure formation processes in synthetic polyamides during solidification from melts, and of structural transformations of these polyamides on heating. We based this work on concepts of the crystalline nature of synthetic polyamides which were demonstrated in a number of papers on structure and mechanical properties [4], including our own work [5], and in which, we believe, the possibility of preparing caprolactam in two structural modifications, crystalline and amorphous, was shown for the first time. It was of great interest to verify these results by the method described.

TABLE 1
Temperature Regions of Exo- and Endothermic Effects of Polyamide Fiber.

Treatment of fiber	Temperature region (°C)					
	First endothermic effect		Second endothermic effect		Exothermic effect	
	beginning	end	beginning	end	beginning	end
Drawn fiber, conditioned in air	103	126	206	217	180	189
Undrawn fiber, conditioned in air	90	122	196	216	179	190

Note. The results are mean values of 5-7 experiments with an accuracy of 2.5-3.5°.

* See Plate, page 309.

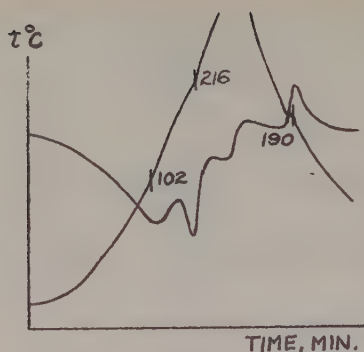


Fig. 2. Heating and cooling curve for drawn polyamide fiber.

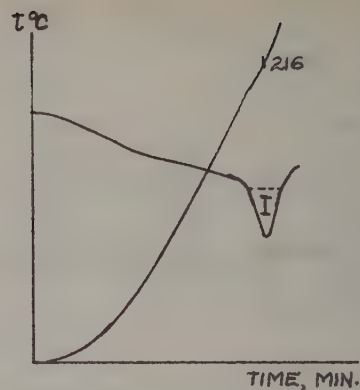


Fig. 3. Curve for the secondary heating of polyamide resin.

From the practical standpoint, the problem consisted of the elucidation of the following questions: 1) what thermal processes take place when the polyamide is heated, their sign, reversibility, and temperature region; 2) relation of these thermal processes to their kinetics; 3) quantitative evaluation of the absolute values of the thermal effects which take place on heating and cooling of the polyamide.

A series of curves was obtained in studying the structure of polycaprolactam. Fig. 2 shows the heating and cooling curve for air-dry polyamide fiber. Comparison of the curves for drawn and undrawn fibers showed these curves to be identical.

The curves of Fig. 2 show two endothermic effects in the heating region and one exothermic effect in the cooling region. It was thought that the first endothermic effect is due to removal of water from the polyamide, and the second to its fusion and transition into the viscofluid state. The single exothermic effect on the cooling curve must be due to the crystallization process which took place during cooling of the polyamide.

Table 1 shows the results of determinations of the temperature regions of these effects on the heating and cooling curves for polyamide fiber.

Since the accuracy of the temperature measurements was $2.5-3.5^\circ$, it follows that the temperature regions of the removal of water, and of fusion are different for drawn and undrawn fibers.

Fig. 3 shows the curve for a second heating of the resin obtained after remelting of the polyamide fiber. It is seen from this thermogram that when freshly remelted solidified resin is heated, only one endothermic process takes place, in the same temperature region as in the primary heating curve. Comparison of three thermographic curves (Fig. 2 and 3); primary heating curve for the polyamide, secondary heating curve of the same polyamide, and the cooling curve, shows that the process associated with the appearance of the first thermal effect in the period of the experiment is irreversible and is due to the removal of water from the polyamide.

It is most interesting that as the result of these experiments the crystallization temperature of synthetic polyamide has been established; as was to be expected from the theoretical laws of crystallization of linear polymers, this temperature is not a single point, but a temperature range which is considerably below the range for the transition of the polyamide into the viscofluid state ("melting").

If the experimental error is taken as $2-3^\circ$, the reliability of the observed gap of $20-25^\circ$ between the crystallization temperature and transition into the viscofluid state is not open to doubt. This fact is to be explained by kinetic hindrances of crystallization in linear polymers, which lead to a delay of the molecular regrouping necessary to establish spatial orientation.

On the basis of the observed kinetic hindrances in the crystallization process, it was of interest to determine the part played by this factor in relation to the heating process, itself. With the thermographic method it was possible to follow the solidification and fusion of the polyamide at different rates of heating.

TABLE 2
Temperature Region of Melting of Polyamide Fiber at Two Rates of Heatings

Rate of heating in deg. per minute	Temperature region of melting, deg.
3-5	206-216
20-25	216-232

Note. Mean values from 5 experiments were taken.

Fig. 4. shows the heating curve for the polyamide at a heating rate of 20-25° per minute. Comparison of the heating curves obtained at heating rates of 3-5°

per minute and 20-25° per minute shows that at higher heating rates the region of "melting" and of transition into the viscofluid state is displaced in the direction of higher temperatures.

The thermogram in Fig. 4, obtained at a higher rate of heating, shows three endothermic peaks at temperatures of 70-80, 150-160, 230-240° C. It might be expected that at higher heating rates the temperature region of the transition would be displaced in the direction of lower temperatures. However, all these effects were not reproduced on thermograms obtained on a second heating at a rate of 3-7° per minute for a specimen initially heated at a rate of 20-25° per minute: the thermogram for the second heating of a previously rapidly heated polyamide resin (Fig. 5) showed only one remaining effect, in the temperature range of 206-216°. Therefore, it must be considered that at a heating rate of 20-25° per minute the heating range is the effect in the temperature region of 216-232°.

Thus, the dependence of the temperature region of "melting" and of the transition of the polyamide into the viscofluid state on the rate of heating deviates from the usual behavior of low molecular crystalline substances. To investigate a possible connection of this phenomenon with the pyrometric method of temperature measurement, we plotted heating curves for naphthalene and tin at increased heating rates. There was an almost complete absence of any influence of the heating rate on the melting point of these substances.

This effect was then verified for polyamides of different structure. Fig. 6 shows a thermographic heating curve for glass amorphous polyamide in the form of transparent monofil, the structure and conditions of preparation of which are described in the previous paper [5, 1954].

At a heating rate of 3-5°, two endothermic effects are reproduced, but in different temperature regions. The first endothermic effect is in the temperature range of 120-160°, and the second, in 216-224°. One may suppose

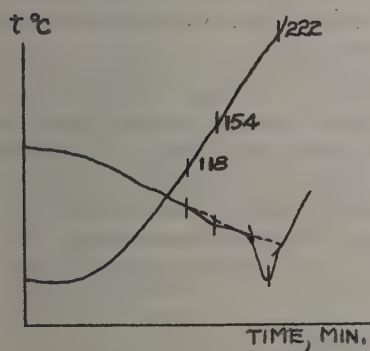


Fig. 6. Heating curve for transparent monofil (amorphous preparation).

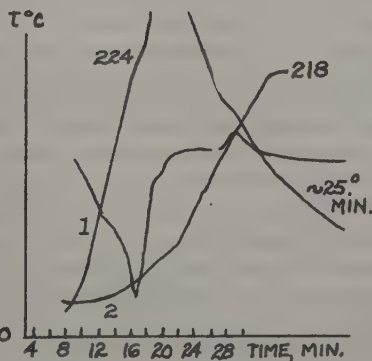


Fig. 7. Heating and cooling curve for "annealed" polyamide fiber (rapid heating).

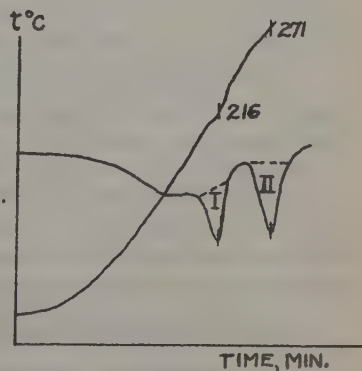


Fig. 8. Heating curve for the polyamide and bismuth in the same sample.

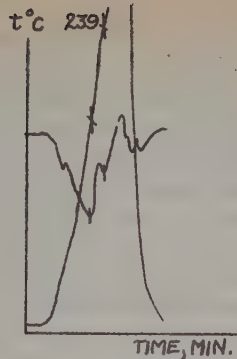


Fig. 4. Heating and cooling curve for polyamide resin (rapid heating and cooling).

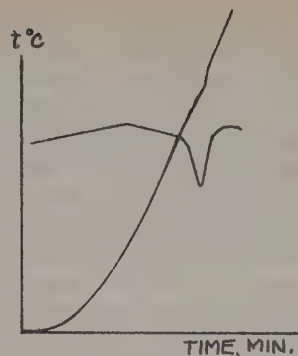


Fig. 5. Curve for a second heating of a resin previously heated rapidly.

that when the amorphous preparation is heated to the temperature of the first endothermic effect, the polyamide passes from the glassy into the highly elastic state. The appearance of the second endothermic effect at 216-224°, is apparently to be explained by transition of the polyamide from the highly elastic into the viscofluid state. On the basis of well-known theoretical considerations this effect should be explained by the fact that the amorphous preparation crystallized after devitrification and heating to 160°, and on further heating to 216° it melted and passed into the viscofluid state. However, microscopic observation in polarized light during heating of the glassy preparation did not disclose any formation of crystals, which is in favor of our supposition. The absence of exothermic effects on these curves also confirms that no crystallization takes place in the specimen. The slight thermal effect of the glassy state transition of the polyamide may be explained by the relatively small number of apparently very weak bonds between the polyamide molecules in the amorphous state, coordination changes of which in close order have little effect on the energy picture of the transition from the glassy to the high-elastic state. The second endothermic effect, as was already noted, may be explained by transition of the polyamide from the high-elastic into the viscofluid state. Clearly, these changes should correspond to a considerable difference in the energy of the polyamide structure, due to further changes, as the temperature increases, of the close order of coordination of the links in the polyamide chains, or to a change in the heat capacity, attributed to the same cause.

The observed latent heat effects in polyamides, within the limits of a single phase state, and our proposed explanations of their causes, are in contradiction to the generally known concepts which relate the existence of such energy changes in the system only to first order phase transitions. However, it was similarly shown in a series of papers [6] with glasses of organic and inorganic origin and with tripalmitin and tristearin, that absorption of heat takes place in the softening region of these substances, as is clearly shown by the differential heating curves. These effects are usually less than the corresponding effects for the fusion of these substances in the crystalline state. The consumption of heat in transitions in one and the same phase is associated with possible changes in the molecular configuration of the substance.

The cooling curves for amorphous specimens of polyamides, one of which is shown in Fig. 7, are practically the same as the cooling curves for the same polyamides with a crystalline structure (Fig. 2), which is quite understandable, as the supercooled specimen passed into a melt on heating and therefore acquired a structure different from the original.

Determination of the Heats of Melting and Crystallization of Polyamide from Thermographic Data

One of the important physical characteristics of a substance is the heat of fusion or the heat of crystallization. We failed to find in the literature any heat of "fusion" of polyamide, but its value was of a definite theoretical and practical interest to us. Determination of the heat of "fusion" of a polymer by the calorimetric method entails a number of experimental difficulties. The use of the thermographic method facilitated the collection of data necessary for calculation of the heat of fusion of the polyamide. For this purpose we used the method proposed by Berg and Anosov [7], which consists of the measurement of the areas of the thermal effects shown by the differential curves for the specimen and a standard, the heat of fusion of which is known from direct calorimetric data. Such substances, used in our experiments, were chemically pure naphthalene, tin, and bismuth, the data for which are shown in Table 3.

The accuracy of the measurements obtained by the method of Berg and Anosov is in the range of 5-10%, and is considerably below the accuracy of the calorimetric method. However, as it was desired to obtain at least an approximate value, it was decided to use the thermographic method of determination.

A number of heating curves for the polyamide and standard were obtained. The heating was carried out in the same sample (definite amounts of the polyamide and standard were placed in the same test tube) in order to eliminate as much as possible the effect of experimental conditions on the thermographic curve. One such curve is shown in Fig. 8. The areas under the differential heating curves of the investigated polyamide and standard substances were determined accurately with a planimeter, and the heats of fusion of the polyamide were then calculated. The calculation was based on the known value of the heat of fusion of the standard substance and on the ratio of the measured areas of the differential curves. The mean value found for the heat of fusion of the polyamide, determined against three standard substances, was found to be 12.50 cal/g.

Table 3 shows the calculation data for the heat of fusion of the polyamide.

The heat of crystallization of the polyamide was determined from the difference between the areas of the thermographic "fusion" curves for crystalline and supercooled amorphous polyamide, and was found to be 0.34 kcal/mole. Despite the approximate nature of the value for the heat of crystallization of polyamide obtained

TABLE 3
Heat of Fusion of Polyamide, Determined by the Thermographic Method.

Standard substance	Heat of fusion of the standard		Area under the differential curve, in units of area		Heat of fusion of the polyamide	
	cal/g	In kcal per mole and g-atom	Standard	Polyamide	cal/g	kcal/mole
Naphthalene	34.7	4.3 kcal/mole	9.5 for 1.00 g	3.5 for 1.00 g	12.6	1.4(mean value)
Tin	13.8	13.8 kcal/g-atom	18.5 for 4.92 g	3.5 for 1.00 g	12.5	
Bismuth	14.1	2.5 kcal/g-atom	5.8 for 1.91 g	2.8 for 1.00 g	12.7	

TABLE 4
Heats of Fusion and Crystallization of Polyamide and Some Crystallizable Substances.

Substance	M.p. °C	Heat of fusion		Heat of crystallization	
		cal/g	kcal/mole	cal/g	kcal/mole
Sodium chloride	804.3	123.5	7.2	123.5	7.2
Stearic acid	64.0	47.6	13.5	47.6	13.5
Polyamide	206-216	12.5	1.4	3.0	0.34

by this method it may be noted that the value is very small in comparison with true crystalline substances. Table 4 shows certain thermochemical data of substances which crystallized well, and also data for polyamide. For these substances the heat of fusion is practically equal to the heat of crystallization.

SUMMARY

1. Synthetic polyamides of the polycaprolactam type crystallize from melts at temperatures considerably below the temperature of transition into the viscous flow state, which is usually erroneously termed the melting point. Two transition temperatures should be distinguished, one of which relates to a first order phase transition, that is, crystallization proper or "fusion", and the other to the transition of the liquid melt into a nonequilibrium supercooled state, which has the properties of a highly elastic body and which therefore does not offer much hindrance to crystallization of the polyamide.
2. Both these transitions are characterized by different thermal effects and take place not at points, but over relatively wide ranges of temperatures.
3. The experimentally demonstrated existence of different temperature regions of crystallization and of transition of synthetic polyamides into the viscofluid state provides a theoretical basis for the possibility of existence of two structural modifications of polyamides: crystalline and amorphous.
4. A thermographic comparison of the thermal effect of transition of crystalline and amorphous polyamides into melts was used to evaluate the molecular heat of crystallization of polycaprolactam, which should be the upper limit of its true value, and which differs from the corresponding values for low molecular substances by more than an order of magnitude.

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PECULIARITIES OF THERMAL EXPANSION OF GELS AND SOLUTIONS OF HIGH POLYMERS

III. TEMPERATURE RELAXATION OF VOLUME IN GELATIN GELS

R. E. Neiman

In communication [1] data were presented on the peculiarities of thermal expansion of gelatin gels. While determining the conditions necessary for the establishment of equilibrium volume at a given temperature, we discovered temperature relaxation effects of the gel volume. Study of these effects also presents an independent interest, since temperature relaxation of volume must be related to the mobility and flexibility of the chain molecules.

The kinetics of the establishment of the equilibrium volume of gels was studied in dilatometers. The gel, placed in the dilatometer, was held before the experiment for twenty-four hours (or, in a number of cases, longer) at a temperature 10° below the temperature of the experiment. The dilatometer was then placed in a thermostat at a definite temperature and the gradual change of the gel volume was observed. The final values of the volumes are the equilibrium values, as they are reached quite reversibly when the gel is taken to the required temperature both from lower and from higher temperatures. The time required for the equilibrium volume to be reached is in most cases measured in hours. Thus, gelatin gels show temperature relaxation of volume.

Fig. 1 shows curves for the kinetics of establishment of equilibrium volume for gels of various concentrations at 25° . These curves give an indication of the observed relaxation processes and of the effect of gel concentration on the kinetics of the process. The volume relaxation of gels and solutions of gelatin was studied at different temperatures. The basic laws which were found are shown graphically in Fig. 2. This figure shows the values of the logarithms of the relaxation periods τ in dependence on $\frac{1}{T}$, the reciprocal of the temperature of the experiment ($T^\circ K$).

The curves in Fig. 2 demonstrate the existence of two different mechanisms of temperature relaxation of volume of gelatin, each of which appears in a definite temperature region. It may evidently be concluded that the break in the curves corresponds with some degree of accuracy to the melting temperature of the gels, which increases with increasing concentration of the latter (from $28-29^\circ$ for 10% gel, to $33-34^\circ$ for 20%, and $35-36^\circ$ for 40%). Below the melting point, when a structural network exists in the gel, the temperature relaxation of volume is due to regrouping of links and of free regions of the chains which takes place on change of temperature. The effect is weakest in 10% gel.

Increase of concentration, that is, increase in the number of local bonds in the gel, leads to a strong increase in interaction between the chains, which results, as is seen from Fig. 1 and 2, in a retardation of the process and a noticeable increase in the relaxation periods. No appreciable change, however, takes place in the angle of inclination of the $\log \tau = f\left(\frac{1}{T}\right)$ curves. This means that the activation energy of the relaxational process of regrouping of links and regions of the chains depends not on the total number but on the nature of the local intermolecular bonds, reversible rupture and restoration of which are possible when the system is in the gel state. These are evidently the least stable bonds. The stronger local bonds, which are responsible for the structural network of the gel, have a higher potential barrier and do not take part in the relaxation process.

The rupture of these local bonds and the disappearance of the structural network which occur during melting of the gel provide an opportunity for mutual displacements and regroupings of the chain macromolecules during

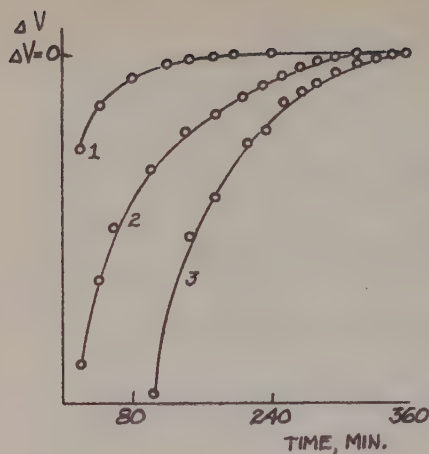


Fig. 1. Kinetics of establishment of equilibrium volume of gelatin gels at 25°C; $\Delta V = V_T - V_0$ is expressed in arbitrary units of the difference between the volume V_T , measured at each given moment, and the final volume V_0 ; 1) 10% 2) 20% 3) 40% gelatin gels.

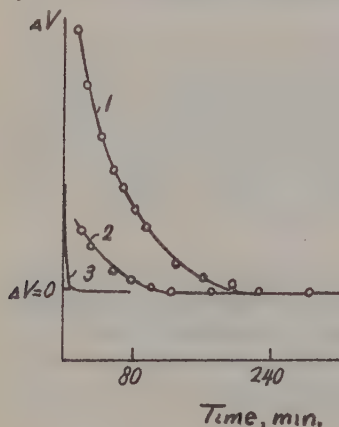


Fig. 3. 20% gelatin gel, prepared with 3 M urea solution at the following temperatures: 1) 0°C; 2) 22°C; 3) from 25 to 38°C.

energy is about 20-23 kcal per arbitrary mole, and above the melting point it reaches about 60-65 kcal per arbitrary mole. In evaluation of these values, it should be remembered that they relate, strictly speaking, to the structural element of the chain (segment) which relaxes as a whole, and which includes a group of bonds which participate in the relaxation process.

These values give a relative measure of the strengths of different types of intermolecular bonds between the chain molecules of gelatin. The first value characterizes the weaker bonds, to reversible rupture of which is due the relaxation process of regrouping of separate links and regions of the chains in the gel without mutual displacement of the macromolecules as a whole. The second value relates to the more stable bonds, responsible for the formation of a structural network in the gel; reversible processes of disruption and restoration of these become possible after melting of the gel, when the corresponding activation energy can be reached.

Fig. 2 also shows the $\log \tau = f\left(\frac{1}{T}\right)$ curve for 20% gel tanned with 3% quinone. This curve has a greater slope than the curves for the other, normal gels, which indicates a certain increase in the activation energy of the

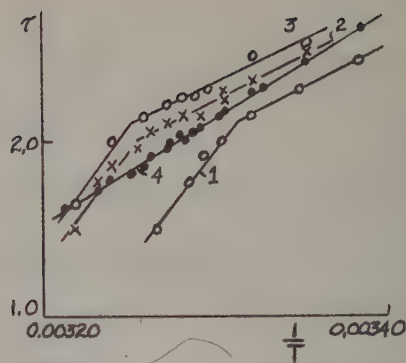


Fig. 2. Curves for $\log \tau = f\left(\frac{1}{T}\right)$: 1) 10%; 2) 20%; 3) 40% gelatin gel; 4) 20% gel, tanned with quinone.

thermal expansion of the solution, in accordance with relaxational laws. As Fig. 2 shows, above the melting point the slope of the curves for $\log \tau = f\left(\frac{1}{T}\right)$ increases, and therefore there is an increase in the activation energy of the relaxation process. This may be explained by the fact that mutual displacements of the bonds are associated with surmounting of the potential barrier of the more stable local intermolecular bonds. Below the melting point these bonds form the stable structural network of the gel, the potential barrier of which is not surmounted during thermal expansion right up to the melting point, and mutual displacements of the macromolecules are impossible. Above this point, mutual displacements of the chains are associated with surmounting of the potential barrier of the same bonds, which do not form a stable network, but are capable of reversible disruption and restoration. Thus, these bonds are also included in the relaxation process, while below the melting point they do not take part in it.

On the basis of experimental data on the dependence of the relaxation periods on temperature, we calculated the activation energy of the relaxation process. Below the melting point of the gel, the activation

relaxation process. The latter may be explained by an increase in the intermolecular interaction by the introduction of new quinoid linkages. The melting point of this gel is displaced in the direction of higher temperatures, and no break in the curve is observed in the interval studied.

We also carried out several experiments with 20% gel prepared with 3 M urea solution. In this gel the melting point is appreciably displaced in the direction of lower temperatures. The region in which the temperature relaxation of volume is observed is also displaced in the same direction. Figure 3 shows the curves for the kinetics of establishment of equilibrium volume of this gel. At 25° and above, relaxation of volume is completely absent, while in normal gels it is shown quite clearly at these temperatures. At lower temperatures a gel prepared with urea also shows volume relaxation.

Kargin, Zubov, and Zhurkina [2] studied mechanical relaxation of protein gels and showed that by the study of relaxation phenomena it is possible to differentiate between processes of flow, that is, of mutual displacement of macromolecules, and their deformation due to regrouping of links and separate regions of the chains; a significant difference between the relaxational behavior of gels and solutions was also found.

On the basis of the above results it may be asserted that the laws of the temperature relaxation of volume of gels also show the existence of two types of processes and, correspondingly, two types of temperature relaxation. One of these is associated with the mobility and mutual displacements of the chain macromolecules (temperature relaxation of volume of the solution), and the other with the flexibility of chains and regrouping of links and regions of the chains (relaxation of volume of the gel). The melting point of the gels may be found from the break in the

$\log \tau = f\left(\frac{1}{T}\right)$ curves with a reasonable degree of approximation.

Thus, investigation of the temperature relaxation of volume of gels leads to conclusions in agreement with the views developed in the papers cited [2].

SUMMARY

1. Temperature relaxation effects of volume for gels and solutions of gelatin were found and studied. The existence of two kinds of relaxation process is shown; one of them is associated with regroupings of links and separate regions of the chains (gels), and the other with mutual displacements of the chain macromolecules (solutions).

2. Breaks on the curves of the logarithms of the periods of temperature relaxation of volume plotted against temperature indicate the transition from gel to solution.

3. The activation energy of the relaxation process provides a comparative measure of the strengths of different types of intermolecular bonds.

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HETEROGENEOUS ION EXCHANGE REACTIONS

I. THE REVERSIBILITY OF ION EXCHANGE REACTIONS ON SYNTHETIC RESINS*

K. M. Saldadze

One of the controversial questions concerning the laws of ion exchange processes is the question of the reversibility of the reaction taking place between the resins and the electrolyte solutions. Walton [1] found in his studies of ion exchange on sulfonated coal that the exchange of Ca^{++} for Na^+ and for H^+ is an irreversible process. The same conclusion was reached by other investigators [2] who studied the exchange reactions of Ba^{2+} and Na^+ , La^{3+} and Na^+ , La^{3+} and H^+ , and who observed hysteresis phenomena in the exchange of ions with different valencies on resins. The hysteresis effect was also observed by Schubert [3] in the exchange of ions with different ions on resins. Soil scientists also state that ion exchange on soils, clays, and permutites is irreversible. Thus, Chernov [4], who studied the exchange of ions of Ba and NH_4 , Ca and K, and Ca and NH_4 in soils, found the process irreversible. Reversibility was also not found by Antipov-Karataev and coworkers [5] in their studies of the exchange of ions of Cu and Ca, Pb and Ca, and Hg and Ca in soils and clays. These authors explain the irreversibility of the process by the non-equivalence of the active adsorption centers on the surface of the adsorbent. On the other hand, several workers [6] assume, without adequate experimental proof, that the ion exchange process obeys the law of mass action, and is thus of a reversible nature. This contradiction led us to study the reversibility of ion exchange reactions which occur between the resin and the electrolyte solution, as reversibility is the main criterion for establishing the applicability of the mass action law to cation exchange reactions.

As an example of an equation for reversible exchange reactions, derived on the basis of the mass action law, we may take Nikolsky's Equation [7]:

$$\frac{g_1^{1/z_1}}{g_2^{1/z_2}} = K \frac{c_1^{1/z_1}}{c_2^{1/z_2}} \quad (1)$$

where c_1 and c_2 are the concentrations of two different ions in solution; g_1 and g_2 are the amounts of the same ions adsorbed; z_1 and z_2 are their valencies; K is the equilibrium constant.

According to this equation, the sorption isotherms for the relationship between the ratio of the adsorbed ions and the ratio of the concentrations of the ions undergoing exchange in the solution, should consist of one straight line for both the forward and the reverse exchange reactions.

EXPERIMENTAL

To investigate the reversibility of ion exchange processes, three reactions arbitrarily taken as forward, and three as reverse, were studied:

Forward reactions	Reverse reactions
$\text{R Ba} + \text{MgCl}_2$	$\text{RMg} + \text{BaCl}_2$
$\text{R Ba} + \text{KCl}$	$\text{RK} + \text{BaCl}_2$
$\text{R Zn} + \text{CdCl}_2$	$\text{RCd} + \text{ZnCl}_2$

The experiments were carried out with air-dry sulfo-phenolic resins. In ion exchange reactions on these resins, only the sulfonic groups in them take part. The sorption capacity of the resins on their sulfonic groups was 1.42 mg-equiv/l. The sulfonic groups of the resins were saturated with cations in such a way that no hydrogen ions bound to the sulfonic groups remained in the resin. An exception was the case of resins saturated with zinc or cadmium, in the saturation of which the hydrogen ions which remained in the resin bound with the sulfonic groups were taken into account.

The resins remained in contact with the solutions, which had constant ionic strength (0.05-0.075) for 3-4 days, till complete equilibrium was established. The temperature was maintained in the range of 18-20° during the

* E. A. Bozhevolnaya and V. V. Avstrielevskaya participated in the experimental work.

experiments. After equilibrium was reached, both cations were determined polarographically, both in the equilibrium solution and in the resin. The experimental results were then examined with the aid of equation (1). The results of this are shown graphically, in the form of isotherms both for the forward and the reverse reactions in Figures 1, 2, and 3.

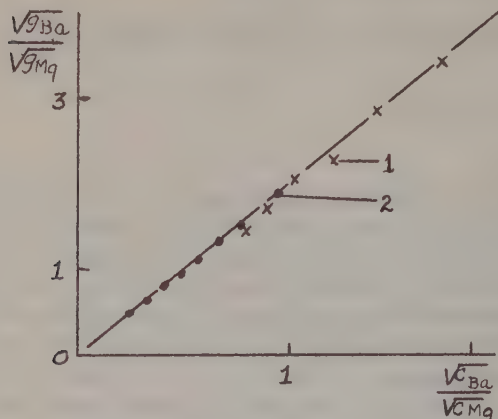


Figure 1. Ion exchange isotherm: 1) Ba and Mg; 2) Mg and Ba on sulfo-phenolic resin.

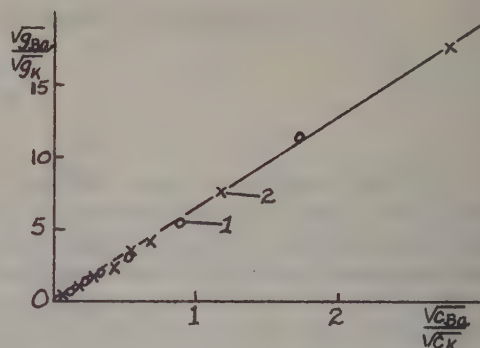


Figure 2. Ion exchange isotherm: 1) K and Ba; 2) Ba and K on sulfo-phenolic resin.

the origin. The linearity of the isotherms shows that the equilibrium constants are of a constant value for each reaction.

It may be concluded from the results in Figures 1, 2, and 3 that the exchange of cations of alkali and alkali earth metals, with equal and different valencies, and also of bivalent zinc and cadmium, which takes place according to the equation $RM_1 + M_2 \rightleftharpoons RM_2 + M_1$ strictly obeys the reversibility laws, and no hysteresis takes place. Thus, the views of the American authors concerning the irreversibility of exchange reactions, particularly of cations of different valencies on resins, are erroneous. It is also improbable that the exchange of ions of different valencies on soils and clays is always an irreversible process.

Nevertheless, irreversibility of ion exchange reactions on synthetic resins is observed if they are accompanied by other processes. For example, in the contact of sulfo-phenolic resins with potassium permanganate solutions, as the result of a reduction process, heptavalent manganese is reduced to quadri- and trivalent. The process is also not reversible in the case of contact of sulfo-phenolic formaldehyde resins with solutions of silver nitrate and mercuric nitrate, and solutions of salts of trivalent iron, where the silver and mercury ions are reduced to the metal, and trivalent iron to bivalent. Reversibility of the ion exchange process can also hardly be expected if it is accompanied by molecular sorption, when the equivalence of ion exchange is disturbed; or in cation exchange when the resin is saturated with a metal which forms a stable complex or a colloidal compound with the solutions of salts or acids in the liquid phase. The latter occurs in the separation of rare earth elements, when the adsorbed rare earth metals are eluted with ammonium citrate or other complex formers, which form complexes with the rare earth metals at a definite pH value of the solution. A similar effect is observed in the exchange of Cu^{2+} or Fe^{3+} in the resin by Na^+ from sodium citrate solution, when Cu^{2+} or Fe^{3+} , which pass into solution at solution pH above 2.5, form a stable complex.

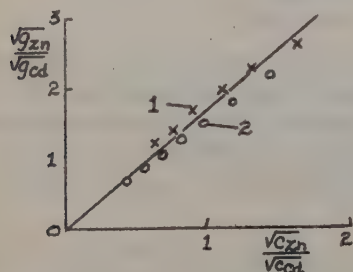


Figure 3. Ion exchange isotherm: 1) Zn and Cd; 2) Cd and Zn on sulfo-phenolic resin.

Consequently, ion exchange reactions on synthetic resins may be irreversible if the equivalence rule is not obeyed in these reactions due to the presence of other processes: reduction, complex formation in the solid or the liquid phase, or the formation of colloids and suspensions.

In ion exchange between resins and solutions of strong electrolytes, where ion exchange strictly obeys the equivalence laws, the cation exchange reaction is reversible.

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THERMODYNAMICS OF SWELLING OF NATURAL AND SODIUM-BUTADIENE RUBBER IN BINARY MIXTURES

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The thermodynamics of ternary systems including high polymers has started to be built up in very recent years. In a number of papers [1] calculations are made of the thermodynamic functions of high polymer plus two low-molecular liquid systems. However, in papers devoted to studies of swelling in binary media [2] no attention is given to the experimental determination of the thermodynamic functions in the high polymer phase. Thus, at the present time the ability of a theory to predict the values of degrees of swelling is almost the sole criterion of the validity of theoretical concepts in the field of thermodynamics of swelling in binary media. There are very scanty data [3] by which it is possible to verify the extent to which a given theory predicts the distribution of the low molecular components between the two phases, and data are almost completely lacking for evaluating the degree of accuracy with which theoretical calculations give the free energy components—enthalpy and entropy.

It is evident that the strict theory of the thermodynamics of ternary systems including high polymers must be based on reliable experimental data. In our view an undesirable gap exists at the present time between experimental study of the thermodynamics of ternary systems including high polymers, and the theoretical treatment of this problem.

In the present investigation a study was made of the partial molal thermodynamic functions (free energy, enthalpy, and entropy of the low molecular components) in the systems natural rubber vulcanizate—benzene—lower alcohols, and in the systems sodium butadiene rubber vulcanizate—benzene—lower alcohols (from methyl to *n*-butyl inclusive) in equilibrium with binary solutions.

EXPERIMENTAL

Swelling was studied in small flasks of 100 ml capacity, with well-fitting ground stoppers fitted with glass hooks for suspending the specimens in the saturated vapor phases; the ground glass joints of the flasks were lubricated with graphite.

The same volume of solution, 10 ml, and approximately the same weight (~ 200 mg) samples of rubber of equal dimensions were used in the experiments. In other respects the experimental procedure, including the preliminary washing of the rubber and interferometric analysis of the solution in the polymer phase, does not differ from the procedure described in the earlier papers [4].

The experiments described in the present paper were carried out at 20 and 50°. The thermostat consisted of an air oven with double walls, fitted with a contact thermometer from a Höppler thermostat, relay, and an electric lamp used as a heater. The temperature fluctuations did not exceed $\pm 0.5^\circ$ at 20 and $\pm 1^\circ$ at 50°. As, according to our experiments, the temperature coefficient of variation of the molal fraction of alcohol in the polymer phase dN_2/dT does not exceed 0.002, while the accuracy of analysis of the composition is approximately 5%, this accuracy of temperature control is quite sufficient, as the transition from the activities of the components of the binary equilibrium solution to the activities of the components in the polymer phase, with the method used in the present study, is based exclusively on the curve for the equilibrium between the polymer and the binary solution. The flasks with the specimens were thoroughly darkened.

Swelling studies were made on vulcanizate of natural rubber with the following composition: rubber, 100; technical stearin, 1; Neozone D, 1; Captax, 1.5; zinc oxide, 5; sulfur, 2. And sodium butadiene rubber vulcanizate (plasticity value 35) with the composition: synthetic rubber, 100; Captax, 0.25; DPG, 2; zinc white, 2; technical stearin, 1; machine oil, 23; oleic acid, 0.5; rosin, 0.5; lamp black, 120; and sulfur, 2.5. The natural rubber was vulcanized in a hydraulic press at a pressure of 100 atm and temperature of 132° for 50 minutes, while the butadiene rubber was vulcanized in a vulcanization autoclave at a pressure of 4 atm and temperature of 130° for 15 minutes.

Isochronic swelling curves were studied for all the systems in the time range of 30 to 2000 hours, including interferometric analysis of the solution in the polymer phase. As an example, Figures 1 and 2 show the results of

such a study in the form of graphs for degree of swelling against time, and molal fraction of alcohol in the polymer phase (N_2^n) against time (t) for the system butadiene rubber-benzene-methyl alcohol.

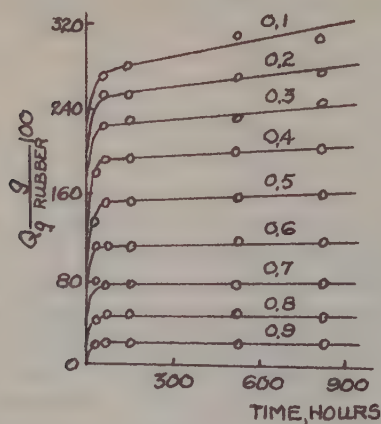


Fig. 1. Kinetic curves for the system butadiene rubber-benzene-methyl alcohol. The numbers on the curves represent values of N_2 .

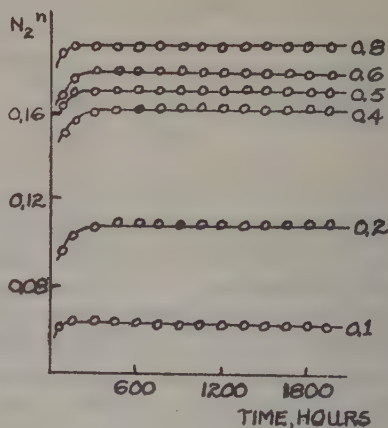


Fig. 2. Curves for the molal fraction of alcohol in the polymer phase (N_2^n) against time for the system butadiene rubber-benzene-methyl alcohol. The numbers on the curves represent values of N_2 .

It is seen from Figure 1 that the second slow stage of swelling is shown particularly clearly in dilute solutions of alcohol. Figure 2 shows that in the first stage of swelling the mole fraction of alcohol in the polymer phase increases with time, and in the second state becomes practically independent of time. The equilibrium swelling values were found by Scott's method [5], by extrapolation of the linear regions of the swelling curves, corresponding to the slow stage, to zero time. The degrees of swelling found in this way are shown in column 3 of Table 1. These equilibrium values correspond to the time in which the composition of the solution in the polymer phase becomes constant, as can be easily seen by comparing Figures 1 and 2.

Since the slow stage of swelling is accompanied by oxidative degradation of the polymer, the molal fraction of alcohol in the polymer phase should slowly increase due to the increase of the polarity of the polymer. Such an increase of the molal fraction of the alcohol in the polymer phase with time is in fact observed for natural rubber vulcanizate, as is shown in Figure 3, which gives curves for the molal fraction of the alcohol in the polymer phase (N_2^n) against time (t) for the system natural rubber-benzene-*n*-butyl alcohol.

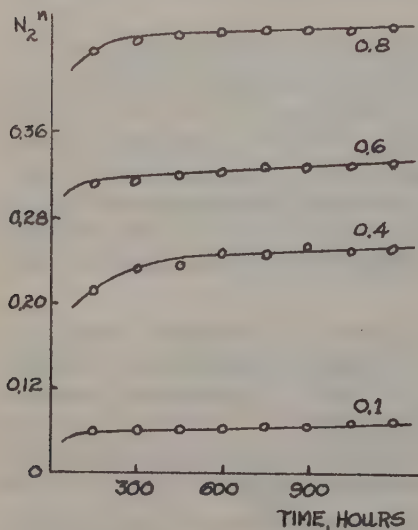


Fig. 3. Curves for the molal fraction of alcohol in the polymer phase against time, for the system natural rubber-benzene-*n*-butyl alcohol. The numbers on the curves represent values of N_2 .

As the increase of the molal fraction of the alcohol in the polymer phase with time is evidence of increasing polarity of the polymer, the data shown in Figure 3 provide experimental confirmation of the fact that the slow stage of swelling is accompanied by oxidative degradation.

A slow increase of the molal fraction of the alcohol with time in the polymer phase is not observed in the swelling of sodium butadiene rubber. This is explained, on the one hand, by the fact that sodium butadiene rubber has a lower molecular weight, and on the other, by the fact that the double bonds, of the 1-2 type in the side chains are less sensitive to oxidizing agents [6]. It is known from the work of Dogadkin [7] that the rate of degradative solution of butadiene polymers is a linear function of the content of 1-4 structure in the polymer.

The much slower oxidation during the swelling of sodium butadiene rubber vulcanizate may be illustrated by the results of the following experiments. Specimens of natural and butadiene rubber were swollen for 14 days in saturated benzene vapor. At the end of that time the specimens were taken to constant

weight in a vacuum desiccator, and were then again swollen for 14 days and taken to constant weight. The increase in the weight of natural rubber vulcanizate in 28 days was 0.0095 g per 1 g, and for the butadiene rubber vulcanizate the increase was 0.0015 g. The increase in the degree of swelling in the second fortnight was 6.6% for natural rubber and 0.3% for butadiene rubber.

Values of the Partial Thermodynamic Functions of the Low Molecular Components in the Polymer Phase

Equilibrium swelling at 20 and 50° was studied. The corrected values for the activities of the components in binary mixtures of benzene-alcohols were calculated from cryoscopic data on heats of dilution with the aid of known thermodynamic relationships. The method of making the calculation was described previously [8]. The values obtained for the activities of the alcohols were recalculated in such a way that the values for the pure alcohols were equal to unity. Thus, for both components of the binary solutions, the pure components were taken as the standard state. With such standardization of activities, their values for a given component are equal in all coexisting phases.

Further, with the aid of curves for the composition of the solution in the polymer phase against the composition of the equilibrium binary solution, the activities of the low molecular components in the polymer phase in relation to the composition of the swollen polymer were determined. The partial molal free energies of the components in the polymer phase were calculated from the equations:

$$\Delta \bar{F}_1 = RT \ln a_1. \quad (1)$$

$$\Delta \bar{F}_2 = RT \ln a_2. \quad (1a)$$

The mean values of the partial molal enthalpies of the low molecular components in the temperature range 20-50° were found by integration of the equations:

$$\frac{d(\Delta \bar{F}/T)}{dT} = -\frac{\Delta \bar{H}}{T^2} \quad (2)$$

The mean values of the partial molal entropies of the components were calculated from the equations:

$$\Delta \bar{S}_1 = \frac{\Delta \bar{H}_1 - \Delta \bar{F}_1}{T} \quad (3)$$

$$\Delta \bar{S}_2 = \frac{\Delta \bar{H}_2 - \Delta \bar{F}_2}{T} \quad (3a)$$

The values so found for the thermodynamic functions of the low molecular components in the high polymer phase for the systems natural rubber-methyl alcohol-benzene, natural rubber-*n*-butyl alcohol-benzene, and synthetic rubber-*n*-butyl alcohol-benzene are shown in Table 1.

Discussion of the Experimental Results

The selective nature of absorption of the solution components, which may be characterized by the deviation of the curve for the mole fraction of the alcohol in the polymer phase against the mole fraction of the equilibrium solution from the straight line joining the points $N_2^n = 0$ and $N_2^n = 1$, is most strongly expressed in systems with methyl alcohol and decreases in the direction of systems with *n*-butyl alcohol. Thus, for a given polymer, the selectivity of absorption decreases in the same direction as the decrease in the densities of cohesion energy of the alcohols. Comparison of the capacities for selective absorption of the two polymers studied shows that (for the same alcohol) the vulcanizate of butadiene rubber has greater selectivity of absorption than natural rubber vulcanizate.

Figure 4 shows the initial regions of the curves for the degree of swelling against composition, for systems with natural rubber.

It is seen by comparing the curves in Figure 4 and columns 1 and 2 of Table 1 that the maxima on the isothermal equilibrium curves obey Konovalov's law. The maximum is most pronounced on the isothermal equilibrium curve for the system natural rubber-benzene-methyl alcohol, and is found at $N_2 = 0.05$. As the molecular weight of the alcohol increases, the height of the maximum decreases, and the composition at which it is found is displaced in the direction of more dilute solutions of the alcohol. In the case of butadiene rubber, the maxima are displaced in the direction of benzene.

The values of the partition coefficients of the alcohol K_2 and benzene K_1 between the high polymer and the binary solution may be determined for both polymers from the initial slopes of the curves $N_2^n - N_2$ for $N_2 = 0$ and $N_2 = 1$ respectively. The values of these coefficients are shown in Table 2.

TABLE 1

Values of Thermodynamic Functions of Low Molecular Components in the High Polymer Phase

N ₂ solution	N ₂ polymer	Q mg g rubber	Q ₁ mg g rubber	Q ₂ mg g rubber	$-\Delta\bar{F}_1^{20^\circ}$ cal mole	$-\Delta\bar{F}_1^{50^\circ}$ cal mole	$\Delta\bar{H}_1$ cal mole	$-\Delta\bar{F}_2^{20^\circ}$ cal mole	$-\Delta\bar{F}_2^{50^\circ}$ cal mole	$\Delta\bar{H}_2$ cal mole	$\Delta\bar{S}_1$ cal deg·mole	$\Delta\bar{S}_2$ cal deg·mole
1	2	3	4	5	6	7	8	9	10	11	12	13
Natural rubber-benzene-methyl alcohol												
0.0	0.0	3274	—	—	—	—	—	—	—	—	—	—
0.020	0.024	3661	3633	28.4	8	10	4	480	780	1500	0.045	5.74
0.040	0.045	3637	3591	45.9	15	18	8	375	560	1250	0.08	5.22
0.060	0.058	3682	3619	62.6	20	22	17	310	450	1060	0.12	4.72
0.080	0.070	3614	3545	68.6	22	28	36	270	385	920	0.16	4.10
0.100	0.082	3501	3391	110.4	25	34	56	240	335	780	0.23	3.52
0.200	0.118	3059	2917	142.6	35	53	154	175	225	350	0.47	1.80
0.300	0.150	2513	2353	160.1	45	66	220	149	180	125	0.72	0.97
0.400	0.175	1984	1822	162.5	52	80	266	130	152	60	1.00	0.66
0.500	0.190	1497	1371	125.9	60	94	303	122	135	32	1.24	0.48
0.600	0.198	1087	974	112.7	75	120	332	110	115	25	1.50	0.36
0.700	0.212	734	646	88.2	142	195	356	85	87	20	1.76	0.26
0.800	0.240	456	397	59.7	287	350	374	57	60	18	2.02	0.17
0.900	0.325	240	196	43.1	615	710	386	35	35	15	2.52	0.10
0.920	0.375	175	135	40.4	750	850	388	30	30	10	2.72	0.08
0.960	0.600	107	61.8	45.8	1120	1250	391	18	18	5	3.50	0.05
0.980	0.760	77.3	39.9	37.4	1650	1740	393	12	12	—	—	—
1.000	1.000	32.8	—	32.8	—	—	—	—	—	—	—	—
Natural rubber-benzene-n-butyl alcohol												
0.0	0.0	3274	—	—	—	—	—	—	—	—	—	—
0.020	0.022	3391	3320	71.5	12	20	52	1080	1600	2840	0.23	14.40
0.040	0.037	3358	3241	117.6	21	32	100	750	1080	2350	0.42	10.50
0.060	0.050	3300	3142	158.6	26	43	135	620	870	1930	0.58	7.30
0.100	0.077	3104	2875	229.5	37	62	210	512	650	1140	0.84	5.28
0.200	0.133	2605	2274	331.3	60	97	340	435	525	420	1.28	2.92
0.300	0.182	2130	1760	369.8	80	126	435	380	440	225	1.63	2.10
0.400	0.228	1688	1316	371.3	100	155	505	328	372	132	1.96	1.60
0.500	0.272	1312	968	343.3	126	200	555	275	310	80	2.240	1.25
0.600	0.317	931	646	285.3	170	244	585	222	252	50	2.49	1.00
0.700	0.375	620	394	225.3	240	325	600	170	192	38	2.77	0.78
0.800	0.444	382	217	165.3	385	485	630	115	132	30	3.20	0.60
0.900	0.603	205	84.0	121.3	690	815	710	58	70	22	4.60	0.43
0.940	0.669	158	54.0	104.0	940	1120	840	35	42	20	6.02	0.36
0.980	0.862	99.8	14.3	85.5	1510	1950	1250	15	17	17	9.50	0.32
1.000	1.000	104.7	—	104.7	—	—	—	—	—	—	—	—
Sodium butadiene rubber-benzene-n-butyl alcohol												
0.0	0.0	2960	—	—	—	—	—	—	—	—	—	—
0.020	0.018	3022	2950	72	12	20	55	1080	1600	2290	0.24	11.0
0.040	0.036	2985	2865	120	21	32	105	750	1080	1970	0.45	9.92
0.060	0.048	2910	2760	150	26	43	150	620	870	1650	0.60	8.00
0.100	0.075	2830	2620	210	37	62	220	512	650	1010	0.87	4.48
0.200	0.140	2528	2220	308	60	97	350	435	525	380	1.30	2.70
0.300	0.195	2300	1880	420	80	126	425	380	440	190	1.64	1.92
0.400	0.248	1875	1450	425	100	155	490	328	372	122	1.96	1.52
0.500	0.295	1500	1090	410	126	200	532	275	310	74	2.27	1.20
0.600	0.336	1070	720	350	170	244	560	222	252	54	2.60	0.96
0.700	0.377	730	460	270	240	325	580	170	192	40	2.92	0.77
0.800	0.438	462	250	212	385	485	602	115	132	30	3.44	0.60
0.900	0.550	282	130	152	690	815	684	58	70	25	4.70	0.46
0.940	0.670	212	70	142	940	1120	890	35	42	22	5.70	0.42
0.980	0.8650	158	30	128	1510	1950	—	15	17	—	—	—
1.000	1.000	128	—	128	—	—	—	—	—	—	—	—

TABLE 2

Values of Partition Coefficients of Alcohols and Benzene Between the High Polymer and the Binary Solution

Alcohols	Natural rubber						Buradiene rubber						
	K ₂	K ₁	-ΔF	ΔH	ΔH ⁿ	ΔS	K ₂	K ₁	-ΔF	ΔH	ΔH ⁿ	ΔS	Q
	1	2	3	4	5	6	7	8	9	10	11	12	13
Methyl alcohol	1.25	12.50	130	-1600	1900	-5.0	1.15	20.00	81	-1550	1950	-5.0	3500
Ethyl alcohol	1.15	10.50	81	-1500	2200	-4.8	1.00	14.30	0	-1520	2180	-5.2	3700
n-Butyl alcohol	1.00	7.30	0	-400	3500	-1.4	0.90	8.70	-58	-900	3000	-3.3	3900

Examination of the data in Table 2 shows that in each of the systems studied natural rubber shows a higher value of the partition coefficient of the alcohol and correspondingly a lower value of the partition coefficient of benzene, than butadiene rubber. Hence it follows that the decrease of free energy in the transfer of a mole of alcohol from an infinitely dilute solution in benzene into the polymer phase is greater for natural than for butadiene rubber. Conversely, the decrease of free energy in the transfer of a mole of benzene from an infinitely dilute solution in alcohol has a higher value for butadiene rubber. This behavior is apparently the consequence of the lower content of double bonds in the principal chains of the sodium butadiene rubber molecules, and a lower capacity for oxidation.

It is important to determine what type of bonds are formed by alcohol molecules with the polar groups in polymers. The change of free energy which accompanies the transfer of a mole of alcohol from an infinitely dilute solution of the alcohol into the polymer, and the partition coefficient of the alcohol between the polymer and the solution, are related by the equation:

$$\Delta F = -RT \ln K. \quad (4)$$

We denote the change of enthalpy in the transfer from the pure alcohol to the polymer by ΔH^N , the change of enthalpy in the transfer from the pure alcohol to an infinitely dilute solution in benzene by Q , and the change of enthalpy in the transfer of a mole of alcohol from the infinitely dilute solution to the polymer by ΔH . From Hess's law, we have

$$\Delta H = \Delta H^N - Q. \quad (5)$$

The values of ΔH^N were obtained by extrapolation to $N_2 = 0$ of the experimental data for the partial heats of dilution of alcohols in the polymer phase (see column 11 of Tables 1 and 2). The values of the heats of solution of alcohols to infinite dilution in benzene were taken from the results in the paper [9]. The values of ΔH calculated from equation (5) are shown in Table 2 for both the polymers studied. The same Table shows changes of entropy in the transfer from an infinitely dilute solution to the polymer, calculated from the equation:

$$\Delta S = \frac{\Delta H - \Delta F}{T} \quad (6)$$

It is seen from column 4 of Table 2 that the transfer of a mole of methyl alcohol from an infinitely dilute solution into natural rubber is accompanied by the evolution of 1600 cal. Approximately the same quantity of heat is evolved in the transfer of a mole of methyl alcohol into butadiene rubber. As this value is considerably less than the energy of the hydrogen bond, the assumption that the alcohol molecules react with the polar groups of the polymers through bonds of the hydrogen type is untenable. The calculations shown in Table 2 confirm the view concerning the dipole-dipole nature of this interaction, put forward earlier by one of the present authors [4]. This view-point is also confirmed by the fact that in the homologous series of alcohols the values of ΔH do not remain constant but decrease with increase of the molecular weight of the alcohol. The explanation may be that as the hydrocarbon chain increases in length, steric hindrances to dipole-dipole interaction increase.

The transfer from an infinitely dilute solution to the polymer is accompanied by a relatively small decrease in entropy. For example, for methyl alcohol the decrease of entropy is 5 cal/deg. mole., while the vapor-liquid transition is accompanied by a decrease of entropy equal to 40.6 cal/deg. mole.. It must be concluded from the entropy change data that the alcohol molecules are attached near the polar groups of the polymer (mainly near the double bonds) in a loose manner, and the mobility of the alcohol molecules in the polymer phase increases with increase of molecular weight. Otherwise it is difficult to explain the increase of entropy between methyl and n-butyl alcohol.

Let us compare the values of the thermodynamical functions of the low molecular components in the phase of the binary solution and in the polymer phase. Figure 5 shows values of the partial molal entropies of benzene and alcohol for both phases as a function of the composition, for the system natural rubber-benzene-n-butyl alcohol.

It is seen from Figure 5 that for a given composition the partial entropy of benzene has the greater value in the polymer phase. There is a further increase (in comparison with the binary solution) in the number of configurations between the benzene molecules and polymer chain segments during the transfer of benzene into the polymer phase. It is also seen from Figure 5 that the transfer of alcohol into the polymer phase is accompanied by a smaller increase of entropy in comparison with transfer into a binary solution of the same composition. This means that in the polymer phase the alcohol molecules are in a more ordered state, due to the fact that they are mainly attached near the polar groups. This leads to a decrease in the number of possible configurations between the molecules of benzene and alcohol in the polymer phase.

As the values of the partial enthalpies of the low molecular components in the polymer phase are positive (heat is absorbed), the decrease of free energy in the sorption by the polymer of low molecular components from the binary systems studied is due entirely to an increase of the entropy of both components. For the case of sorption of single liquids by high polymers this effect is clearly seen in the studies of Kargin and co-workers [10].

It is seen from a comparison of the data of Table 1 that there is a greater increase of the entropy of benzene and a smaller increase in the entropy of the alcohol in butadiene rubber than in natural rubber. The explanation, apparently, is the lower content of free oxidized groups in the butadiene rubber. With a greater content of polar groups in the molecule the probability of a uniform distribution of the alcohol molecules between the polymer chains is greater, and, conversely, a decrease in the number of polar groups should increase the state of disorder in the disposition of the alcohol molecules between the polymer chains.

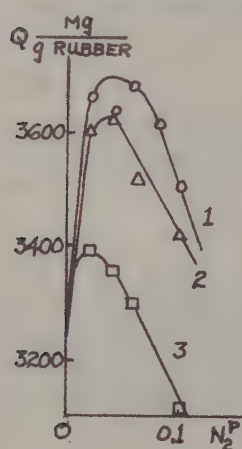


Fig. 4. Initial portions of the curves for the degree of swelling (Q) against the composition of the equilibrium solution (N_2): 1) natural rubber - benzene - methyl alcohol; 2) natural rubber - benzene - ethyl alcohol; 3) natural rubber - benzene - n -butyl alcohol.

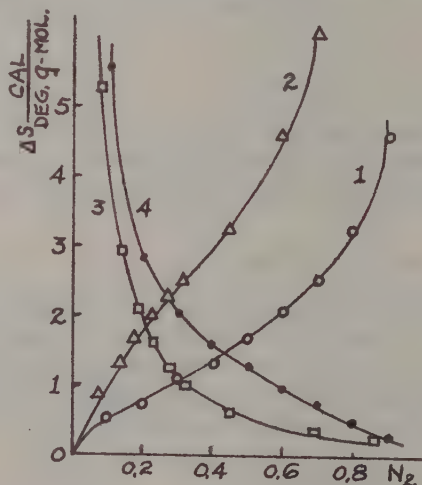


Fig. 5. Curves for the partial molal entropy against the composition for the system natural rubber - benzene - n -butyl alcohol: 1) partial entropy of benzene in solution; 2) ditto, in the polymer; 3) partial entropy of the alcohol in solution; 4) ditto, in the polymer.

alcohol molecules, to an increase in the potential barriers of rotation, to a decrease of chain flexibility, and consequently to a decrease in the entropy of benzene. As the hydrocarbon chain increases in length, the interaction between the polar groups of the alcohol and the polymer becomes weaker, and the differences in the thermodynamic behavior of natural and butadiene rubber almost vanish, as can be seen from the data of Table 2.

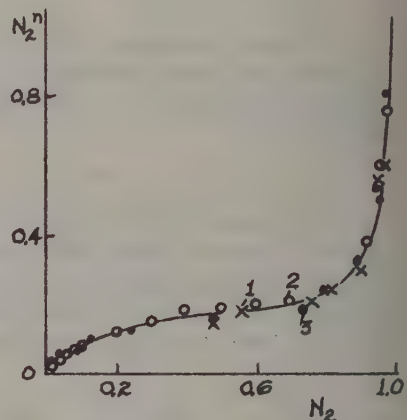


Fig. 6. Distribution in the system benzene - methyl alcohol - polymer: 1) purified natural rubber; 2) natural rubber vulcanizate (without carbon black); 3) rubber loaded with carbon black and chalk.

Increase of the number of polar groups in the polymer leads, because of interaction with the polar groups of the

The question naturally arises whether the form of the curve for the equilibrium between polymer and binary solution depends on the composition of the rubber. Let us compare the data obtained in the present study for the distribution between natural rubber vulcanizate and the system benzene-methyl alcohol, with data obtained by one of us in a study of the behavior, in the same system, of natural rubber vulcanizate containing 35 parts by weight of lamp black and 50 parts by weight of chalk per 100 parts by weight of rubber [4], and also of purified natural

rubber obtained by precipitation with alcohol from benzene solution. The results of the distribution studies with pure rubber and two vulcanizates of different composition are shown in Figure 6, from which it is seen that the distribution between the polymer and the binary solution is determined by the nature of the polymer and is practically independent of the composition of the rubber.

The experimental data of the present study are a further confirmation of Gul's conclusion concerning the necessity of considering the inhomogeneity of the field of force of intermolecular action in rubber [11].

SUMMARY

1. A study was made of the swelling of vulcanizates of natural and sodium butadiene rubber in saturated vapors of the binary systems benzene - lower alcohols (from methyl to n-butyl inclusive) at 20 and 50°, and over the whole composition range of the binary solutions.

2. The general form of the curves for the isothermal equilibrium between the swollen polymer and the binary solution is described by Konovalov's laws.

3. The absorption of a binary solution by the two polymers shows a sharply expressed selective character. The selective character of the absorption is more strongly expressed with higher density of cohesion energy of the alcohol. In natural rubber the capacity for selective absorption is expressed more weakly than in sodium butadiene rubber, which is probably explained by its higher concentration of oxidized groups.

4. The experimental data obtained were used to calculate changes of free energy, enthalpy and entropy for the transfer of a mole of the alcohol from an infinitely dilute solution into the polymer. It follows from these calculations that the interaction of the alcohol molecules with the polar groups of the polymer has a dipole-dipole nature.

5. Transfer from pure benzene to the swollen polymer of a definite composition is accompanied by a greater increase of entropy in comparison with transfer to a binary solution of the same composition. The reverse is true for the alcohols. The increase of entropy of benzene may serve as a measure of flexibility of the polymer chains. The decrease of entropy of the alcohols characterizes the content of free polar groups in the polymer phase.

6. The values of the partial enthalpies of the low molecular components are positive, and therefore the decrease of free energy in their absorption by the polymer is due entirely to increase of entropy.

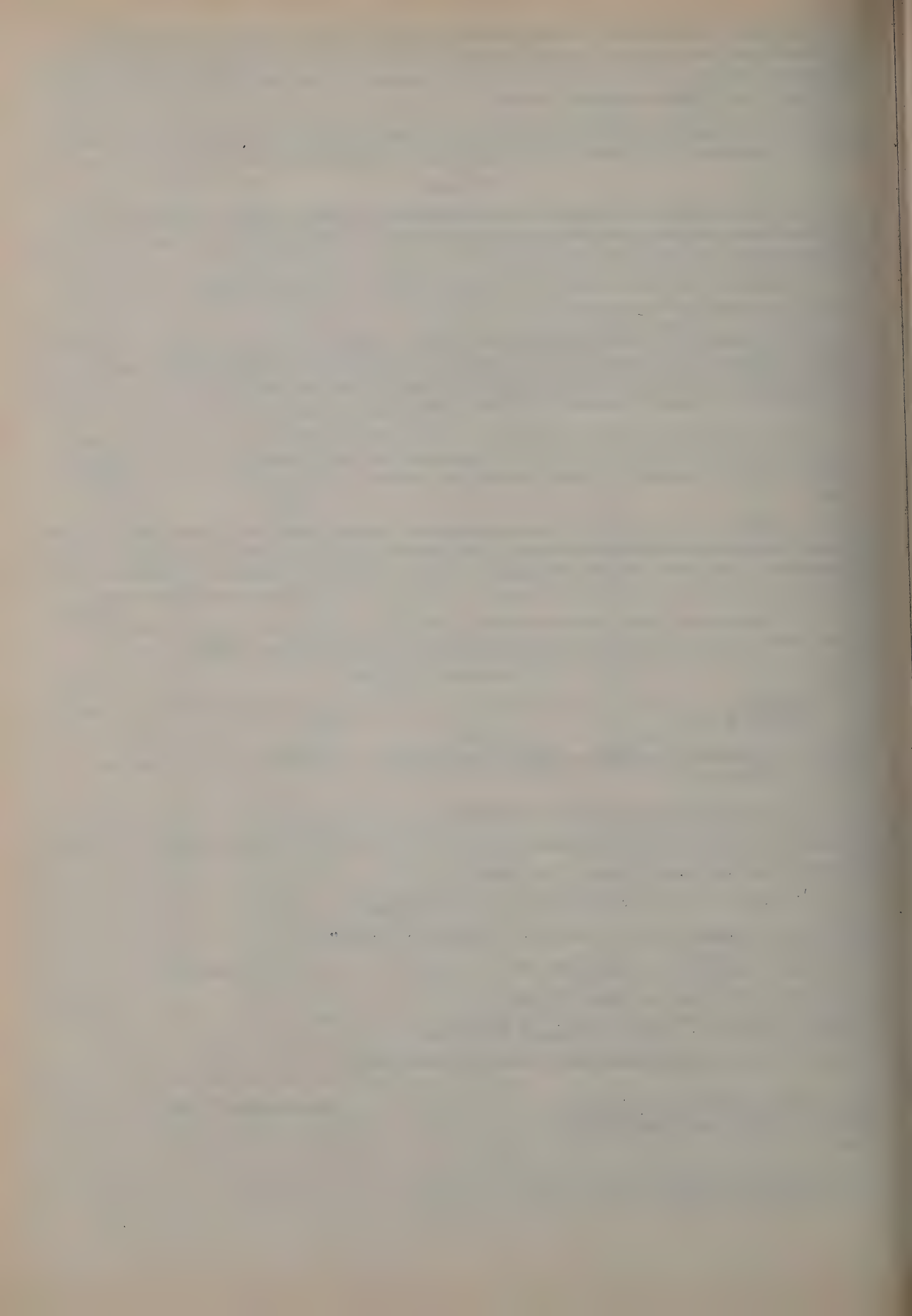
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THE MECHANISM OF EMULSION POLYMERIZATION

III. THE EFFECT OF THE CHARGE ON THE COLLOIDAL PORTION OF THE SOAP SOLUTION ON THE POLYMERIZATION RATE OF STYRENE IN EMULSION

N. A. Fermor and A. B. Peizner

In a previous communication [1] we showed that the rate of emulsion polymerization of styrene in the pH range from 7.0 to 9.5 is considerably less in presence of ammonium oleate than in presence of potassium oleate or of sodium oleate. This cannot be explained by a change in the decomposition mechanism of the initiators, as it is characteristic of all three initiators studied (benzoyl peroxide, potassium persulfate, and the dinitrile of azoisobutyric acid), and it cannot be attributed to the reducing action of ammonia, as one of the initiators used was the dinitrile of azoisobutyric acid. The difference also cannot be explained by a different colloidal solubility of styrene in solutions of ammonium oleate and potassium oleate. When the original oleic acid is 100% neutralized, there is no significant difference between the amounts of styrene colloiddally dissolved in these solutions, while the polymerization of styrene emulsified in it proceeds at different rates. On the other hand, according to Voyutsky [2], the colloidal solubility of hydrocarbons in sodium oleate solutions decreases appreciably with increase of pH even within the limits in which the polymerization rate, according to our data [1] still increases. Finally, the "neutral" solutions of ammonium oleate with excess of ammonia studied by us have almost the same power for colloiddally dissolving hydrocarbons, while it is in that same range of pH that the rate of polymerization of styrene in presence of ammonium soaps sharply increases. Thus, not one of the possibilities* examined here provides a basis for explaining the high rate of polymerization in presence of potassium oleate.

The present authors [3], on the basis of appropriate electrometric and cryoscopic data, made an approximate calculation of the composition of the particles in the soap solutions with variation of pH. From a comparison of the changes in the content of the separate components of these solutions with changes in the rate of polymerization of styrene in them, the following conclusions may be drawn.

The enhanced activity of potassium oleate solutions in regard to polymerization cannot be due to changes in their content of crystalloid soap and total colloid. In fact, the change in the crystalloid content of soap solutions with increase of pH is insignificant, and is not related in any regular manner to change of the polymerization rate of styrene [3, Table 6]. As regards the total colloid content, we have entirely different rates of polymerization in presence of practically equal amounts of total colloids in the solution. It is possible that the total colloid content determines the colloidal solubility of styrene in these solutions, as the colloidal solubility also changes little, but it does not account for the difference in the rate of polymerization.

The position is different in the case of ionic micelles. Changes in the content of charged colloidal particles or the degree of charge of the latter in solutions may apparently play some part in the activity of these solutions, as, even if the activity does not vary completely symbatically, nevertheless these changes, in their character, are similar to changes in the rate of polymerization of styrene in these solutions. This is clearly seen in Figures 1-4. Figures 1 and 2 show variations of the content of ionic micelles and of the rates of polymerization of styrene in solutions of potassium and ammonium oleate (with two different initiators) with changes of pH of these solutions. Figure 3 and 4** show the dependence of the polymerization rate on the concentration of ionic micelles in the soap solutions studied. In all four cases (two emulsifiers and two initiators) this dependence is close to linear. A completely symbatic dependence cannot be expected both because the soap is only one of several rate-determining factors, and also because the composition of the particles in the solutions was determined at 18°, while the polymerization temperature was 60°. The general agreement in the course of the curves for the systems studied, however, apparently indicates the existence of an inner connection between these phenomena.

* No data are available on the relative size of the polymer particles formed in presence of potassium oleate and ammonium oleate. ** The curves in Figures 3 and 4 are based on the data of Figures 1 and 2 of the present communication and also on Figures 7 and 8 of [1] and Table 6 of [3].

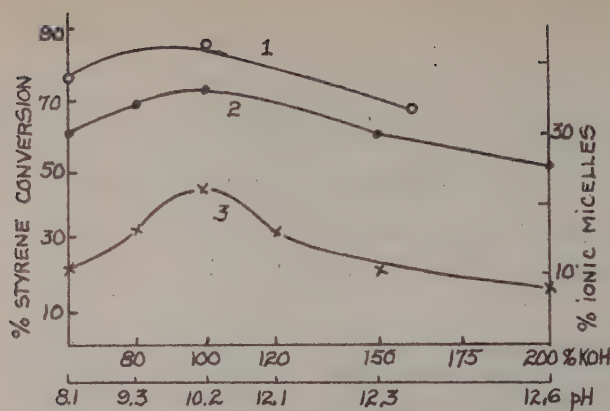


Fig. 1. Rate of polymerization of styrene (curves 1 and 2) and content of ionic micelles (curve 3) in potassium oleate solutions at different pH values; 1) potassium persulfate as initiator; 2) benzoyl peroxide.

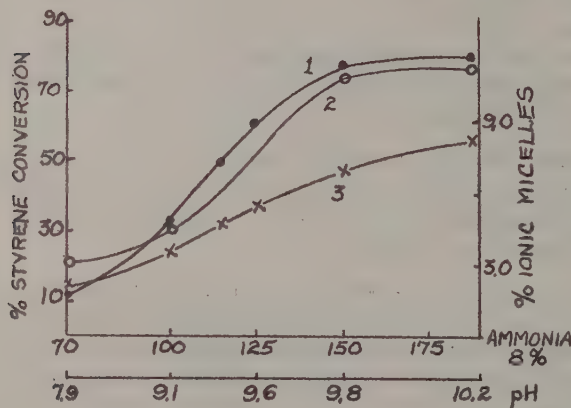


Fig. 2. Rate of polymerization of styrene (curves 1 and 2) and content of ionic micelles (curve 3) in ammonium oleate solutions at different pH values; 1) potassium persulfate as initiator; 2) benzoyl peroxide.

this action may lead to their decomposition, with the formation of free radicals or initial active centers (with the participation of monomer molecules). The monomer molecules which, as is known, are also unstable [4] and are capable of polarization because of the relatively easy mobility of their π -electrons, may also become activated on passing through the electrical double layer. In addition, the surface layer is capable of adsorbing different ions and molecules, of retaining them, and of hindering their penetration into the disperse phase. Consequently, the time during which the initiator and monomer molecules remain in the boundary layer, and therefore the action of the forces named above on these molecules, and also the possibilities of their collision and initiation of reaction in this layer, may increase considerably. The electrical double layer should have a particularly powerful action on charged radicals (radical ions, for example, $\text{SO}_4^{\cdot-}$ radicals).

The charge of the colloid may, in the first instance, activate the decomposition of the initiator which, in our view, takes place principally in the boundary layer: for example, when an oil-soluble initiator leaves the droplets or when a water-soluble initiator enters the soap micelle (polymer-monomer particle, droplet, etc). Indeed, at the interphase separation boundary there is a definite difference of potential due to the formation there of an electrical double layer, consisting of an adsorptional and a diffusional layer, the boundaries of each being determined by the disposition of the negative and positive ions in the double layer. On passing through such a double layer, the molecules of the initiator (and also of the monomer) are subjected to the action of variable stresses and different charges, which leads to their deformation and therefore to activation. In the case of the initiators, in view of their great instability, it is natural to expect that

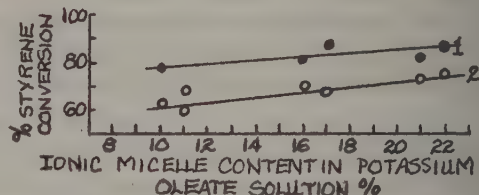


Fig. 3. Dependence of the rate of polymerization in 4% potassium oleate solution on the ionic micelle content; 1) potassium persulfate as initiator; 2) benzoyl peroxide.

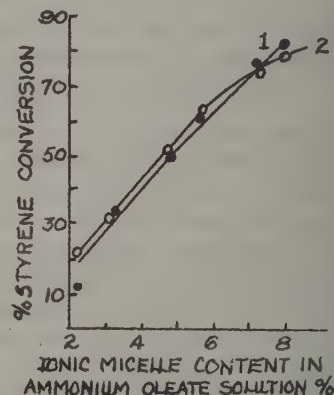


Fig. 4. Dependence of the rate of polymerization in 4% ammonium oleate solution on the ionic micelle content; 1) potassium persulfate as initiator; 2) benzoyl peroxide.

Therefore, it is reasonable to suppose that the degree of charge of the colloidal particles, which determines the structure of the boundary layer and the magnitude of the interphase potential, intensifies their action on the initiator and monomer molecules, and therefore has a significant effect on the polymerization rate. This concept explains quite satisfactorily not only the fact, established by us, of the different rates of styrene polymerization in presence of potassium and sodium oleates, on the one hand, and of ammonium oleate on the other at pH from 7.0 to 9.5, but also explains certain other uncertainties which arise in the examination of existing theories of emulsion polymerization.

Indeed, the micellar hypothesis of emulsion polymerization explains many effects which could not be explained by the hypothesis that the monomer droplets are the sites of polymerization: decrease in the size of the particles during polymerization, the effect of the phase ratio on the polymerization rate, the absence of any dependence between the rate of polymerization and the degree of dispersion of the monomer, the difference in the regulating effect of high molecular mercaptans in bulk* and in emulsion, the nature of changes in the viscosity of the latex and of the vapor pressure above the reaction mixture in the polymerization process, the acceleration of polymerization with increase of emulsifier concentration over a wide range, etc. However, this hypothesis in itself cannot supply answers to certain questions; these include: 1) causes of the greater rate of emulsion polymerization in comparison with bulk polymerization; 2) causes of the lowering of the decomposition temperature of the initiators and acceleration of their decomposition in emulsion; 3) absence of polymerization (or, more correctly, the very small extent of the process) in monomer droplets when initiators soluble in the monomer are used.

Naturally, the high rate of emulsion polymerization cannot be explained simply on the grounds that the reaction occurs in micelles and in polymer - monomer particles, as this only leads to the further question of the explanation of accelerated reaction within the micelles.

The founders of the micellar hypothesis, A. Yurzehnko and Harkins, do not touch on the question of the ratio of the polymerization rates in emulsion and in bulk. Hohenstein, Siggia, and Mark [5] explain the higher rate of polymerization in presence of emulsifiers by a lower activation energy of the initiation reaction in these conditions. They determined the activation energy and the probability factor for the initiation reaction of polymerization of styrene dispersed in aqueous potassium persulfate solution, in presence and in absence of emulsifiers, and they showed that in the absence of emulsifiers the activation energy and the probability factor for this reaction are of the same order as in bulk polymerization, while in presence of emulsifiers the activation energy and the probability factor decrease very considerably (the activation energy by 8000 cal/mole, and the probability factor 10^4 times). The decrease of the activation energy, despite the simultaneous decrease of the probability factor, results in a higher rate of polymerization in emulsion [6, 7]. On the basis of the micellar hypothesis, these workers explain the decrease of the probability factor, that is, the decrease of the number of collisions between the monomer and initiator molecules (or free radicals) in emulsion polymerization in comparison with bulk polymerization, by the relatively low accessibility of the monomer molecules in the micelles to the initiator, due to the protective action of the emulsifier envelopes, the considerable resistance of which to the diffusion of molecules into the micelles is also noted by Harkins [8].**

Hohenstein, Siggia, and Mark, on the assumption that the probability factors for chain transfer or termination are similarly decreased, offer this as an explanation for the generally higher molecular weight of the rubber formed in emulsion. The decrease of the activation energy of the initiation reaction they speculatively regard as the result of orientation and polarization of the monomer molecules within micelles of a highly oriented structure. This explanation, as Khomikovskiy [9] correctly points out, is too general and unsubstantiated.

Corrin [10] attributes the high rate of emulsion polymerization to the increased viscosity of the reaction medium, as the process, in emulsion, occurs almost from the start within polymer-monomer particles, that is, in a viscous solution. Indeed, Medvedev [11] showed as early as 1943, that the polymerization rate of chloroprene increases with increase of viscosity of the reaction medium.

According to the results of Harkins and co-workers [12] the styrene content in polymer-monomer particles which are formed in emulsion polymerization in presence of potassium persulfate decreases slowly and gradually (from 70 to 50%) with increase of degree of conversion in the initial stages (from 6 to 50%), and then, when the polystyrene yield exceeds 50%, decreases rapidly due to the disappearance of the monomer droplets. As the emulsifier concentration increases (from 2 to 10%), the ratio of the weight of monomer to the weight of polymer in the polymer-monomer particles increases (for example, from 1.8 to 2.4 for a polymer yield of 19%). If it is assumed

* This conventional term to denote the polymerization of monomers dissolved in the monomers themselves is adopted by us because of its wide acceptance, brevity, and absence of other, more apt terms.

** This is in agreement with our observations of the rate of colloidal solution of hydrocarbons in static conditions.

that the solubility and swelling power of the polystyrene formed in the monomer is not changed greatly during polymerization and by changes in the emulsifier concentration, then the viscosity of the solution within the polymer-monomer particles should gradually increase up to 50% conversion and then increase sharply, while it should decrease somewhat with increased concentration of emulsifier in the aqueous phase. The increased polymerization rate with increase of emulsifier concentration when the viscosity within the polymer-monomer particles decreases may be explained relatively simply by the fact that acceleration of the reaction due to increase in the number of micelles more than compensates a certain retardation due to decreased viscosity. On the other hand, however, the literature contains no indications of any appreciable acceleration of the reaction at the end of the emulsion polymerization of styrene (even if additional amounts of initiator are added). Of course, this contradiction may be minimized to some extent by an additional assumption of a gradual change in the structure of polystyrene during the polymerization process, but such assumptions cannot be regarded as adequately founded at the present time. Therefore, since it is not possible to establish a clear connection between the rate of polymerization in emulsion and the monomer content in the polymer-monomer particles, it is hardly permissible to consider the viscosity within these particles as the main determining factor for the increased rate of polymerization in emulsion in comparison with bulk polymerization. Apparently, the viscosity of the reaction medium plays a secondary role.

Baxendale and Evans [13] consider that the chief cause of the high rate of emulsion polymerization is the small size of the polymer-monomer particles which at first (at the instant of formation) include only one active macromolecule each, as a result of which termination by recombination is excluded, and can only occur after subsequent coalescence of the separate particles (or on penetration of a new radical into the particle). Even then termination is greatly hindered as the result of the small number of active molecules contained in the aggregates formed. Medvedev and Khomikovskiy [14] also consider the difficulty of recombinational termination in small particles to be one of the main causes of the high rate of emulsion polymerization. It should be noted that, in addition, decrease of particle size increases the effect of the emulsifier coatings on the polymerization process.

When water-soluble initiators are used, it is understandable from the viewpoint of the micellar hypothesis why initiation does not take place within the monomer droplets but is effected outside the droplets (in the aqueous phase, in micelles, and in the polymer-monomer particles), but this is much more difficult to justify when initiators soluble in the monomer are used. At the same time, Rutovskiy [15] showed clearly that in such cases also the greater part of the monomer is polymerized outside the droplets and only a relatively small fraction reacts within the droplets. The high rate of decomposition of the initiator and the relatively low temperature of this decomposition in emulsifier solutions provide the simplest explanation both of acceleration of emulsion polymerization, and of initiation of polymerization outside the monomer droplets (in the micelles or at the interphase boundary, in the electrical double layer) even by initiators which are soluble in the monomer, and this is in good agreement with Rutovskiy's observations [15]; but these facts themselves still need to be explained.

Certain authors [10, 16] attribute the acceleration of initiator decomposition* in presence of emulsifiers to the conversion of the initiators into new and more active compounds under these conditions. Under definite conditions, certain initiators apparently do undergo various transformations before the start of initiation, related in some way or other to the presence of emulsifiers in the system,** but these transformations do not always accelerate polymerization.

For example, Yurzhenko [17] showed that in the emulsion polymerization of divinyl, styrene, and their mixtures, sodium perborate and hydrogen peroxide decompose and disappear from the aqueous phase long before (in some experiments 24 hours before) commencement of noticeable polymerization of the monomers. Yurzhenko considers that a result of the decomposition of these peroxides is the evolution of oxygen, which initiates the process by oxidation of the monomer or of the emulsifiers, as was shown by Talmud [18] in the case of divinyl and oleates. On the other hand, in many well-studied cases the initiator (for example, diazoaminobenzene) decomposes in emulsion also directly into free radicals which initiate the reaction***, and this decomposition is accelerated and occurs at lower temperatures in presence of emulsifiers. Thus, the high rate of emulsion polymerization is apparently due to a combination of factors, of which the most important are: 1) decrease in the possibility of recombinational termination in the small particles of the polymer; 2) acceleration, and lowering of the temperature,

* Both water-soluble (potassium persulfate) and oil-soluble (benzoyl peroxide) initiators.

** The effect of the nature of the emulsifier on the decomposition of initiators was demonstrated in our experiments on the emulsion polymerization of styrene, in particular for the case of benzoyl peroxide in presence of oleates and Nekal at high pH values [1].

*** In some cases the decomposition of the initiators can probably proceed in two directions simultaneously.

of the decomposition of the initiator in emulsion; 3) decrease of the activation energy of the reaction. Up to the present time the causes of the last two effects were not clear, but they are logically explained on the basis of the above hypothesis concerning the effect of the degree of charge of the colloidal emulsifier particles on the rate of emulsion polymerization, the localization of the decomposition reactions of the initiators, and initiation in the boundary layer; they are consequences of destroyed stability of the molecules of the initiator and the monomer in the boundary layer.

Calculations made by Smirnov and Fermor [6] showed that the rate of emulsion polymerization of styrene at 50-60° should be approximately 3 times that of the polymerization in aqueous solution (and also in bulk) as the result of a decreased activation energy and increased probability factor, the values of which were experimentally established by Hohenstein [5]. In general, emulsion polymerization is 20-25 times as rapid as bulk polymerization, as was shown by Dogadkin [19], Carothers [20], and others. There are evidently other factors which accelerate the reaction further 7-8 times. Such factors include: the small size of the polymer-monomer particles, which decreases the probability of recombinational termination [9, 13, 14], and possibly also the increased viscosity within the polymer-monomer particles, chemical reactions with the emulsifier, etc.

Thus, the picture of decomposition of the initiator and of initiation of the polymerization reaction may be presented in the following form. A water-soluble initiator decomposes before penetrating into the micelle in the boundary layer, where it apparently initiates the reaction. An oil-soluble initiator (possibly, in a complex with the monomer) may decompose on leaving the monomer droplet in the boundary layer. If the solubility of the monomer in water is low (the entire picture refers in the first instance to styrene, and then to other monomers which are practically insoluble in water) little or no chain growth occurs in the aqueous phase, and therefore, the active center reaches the micelles, where chain growth takes place. This concept also explains why, as Rutovsky showed, in presence of oil-soluble initiators the process occurs within the droplets only to an insignificant extent (apparently at the rate at which it would take place in absence of emulsifier). Indeed, there are no factors inside the droplets which accelerate the decomposition of initiators or lower their decomposition temperature.

SUMMARY

1. The curves for the dependence of the rate of emulsion polymerization of styrene and the number of ionic micelles on pH of the solution are shown to have definitely a symbatic course. The degree of charge of the colloid in the aqueous phase satisfactorily accounts for the influence of the emulsifier cation on the rate of polymerization of styrene when oleates are used.

2. The supposition is put forward that in studies of the complex mechanism of emulsion polymerization of monomers it is necessary also to take into account the degree of charge of the colloidal portion of the emulsifier solutions, which apparently has a significant effect on the decomposition of the initiator and on the polymerization process as a whole.

In conclusion, the authors consider it their duty to express their gratitude to N. I. Smirnov for valuable advice in the course of this work.

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METHOD FOR THE SIMULTANEOUS DETERMINATION OF THE VOLUME AND WEIGHT COEFFICIENTS OF SWELLING OF GELS FOR THE SAME SPECIMEN

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Either the volumetric or the gravimetric method is used for determining the degree of swelling of gels. Up to the present time no method has been proposed which would give the possibility of determining simultaneously both the volume and the weight coefficients of swelling of gels, with the same specimen both for coherent substances and for powders, and with a sufficient degree of accuracy. By the volume coefficient of swelling is meant the value

$$K_V = \frac{V}{V_0},$$

where V_0 and V are the volumes of the dry and the swollen gel for the same specimen. The weight coefficient of swelling is the value

$$K_P = \frac{p}{p_0},$$

where p_0 and p are the weights of the dry and the swollen gel for the same specimen.

Such a method, proposed by V. P. Mishin and developed by ourselves, may be termed the method of weighing in two inert liquids. The inert liquids used are liquids in which the gel does not swell.

The coefficients K_V and K_P for a given gel are determined as follows. A perforated cup (Figure 1, a) for weighing both the dry and the swollen specimens is made from aluminum foil. This cup is fitted with three thin wires, ending in a hook, which is used for suspending the cup on a torsion balance for weighing. When the degree of swelling of rubber is determined, instead of the cup it is possible to use a wire ring on which pieces of rubber are threaded (Figure 1, b). The determinations are carried out in the same way as with the cup.

The diameter of the gel particles taken was from 1.0 to 1.5 mm. The weights of the gel specimens were from 0.01 to 0.15 g. Weighings on the torsion balance were made with an accuracy of ± 0.3 mg. The swelling liquid is placed in a conical flask of 100 ml capacity. The flask is closed with a stopper carrying a hook for suspending the cup, and with a hole through which passes a stirrer for stirring the liquid during swelling.

The cup, containing a specimen of the gel, taken in the air, is covered with a piece of metal gauze to prevent the particles of the gel from floating, and is lowered into the swelling liquid. The flask with the swelling substance is placed in a thermostat. When the swelling is complete, the cup with the swollen substance is removed from the liquid, the gauze is taken off, and the cup touched with filter paper. This removes most of the adhering liquid from the cup through the perforations. The rest of this liquid is washed away from the surface of the swollen particles by immersing the cup with its contents several times in the weighing liquid. The cup and contents is then transferred to another beaker with the same liquid and is weighed in this liquid. Then the particles of the swollen gel are also weighed in a second liquid.

We thus have the following data: 1) weight of the swollen gel in the first liquid, p_1 , in grams; 2) weight of the swollen gel in the second liquid, p_2 , in grams. The densities d_1 and d_2 of the two liquids are determined previously.

With the aid of these data, the volume and the weight in vacuum of the swollen gel specimen are determined as follows. For the weight of the gel specimen in the first liquid we have



Cup (a) and ring (b) for weighing the gel specimens.

$$p_1 = p - V d_1,$$

where \underline{p} is the weight of the swollen specimen in vacuum. The weight of the specimen in the second liquid is

$$p_2 = p - V d_2.$$

From these two equations we have, when $\underline{d}_2 > \underline{d}_1$

$$V = \frac{p_1 - p_2}{d_2 - d_1}; \quad p = p_1 + V d_1; \quad p = p_2 + V d_2; \quad p = \frac{(p_1 + p_2) + (d_1 + d_2) \cdot V}{2} \text{ g.}$$

In these equations we know the volume occupied by one gram of the dry gel, the density of the first liquid \underline{d}_1 and the density of the second liquid \underline{d}_2 .

We used this method to determine \underline{K}_V and \underline{K}_p for twenty-five different substances. As examples, we give the values of \underline{K}_V and \underline{K}_p for Japanese agar, white beans (in redistilled water) and rubber (in toluene). The values of \underline{K}_V and \underline{K}_p for these substances are shown in Tables 1 and 2.

The following values are shown in Table 1: \underline{p}_0 , the weight of the air-dry specimen of the gel; \underline{V}_0 , the volume of one gram of the air-dry gel; \underline{p}_1 , the weight of the swollen specimen in the first liquid; \underline{p}_2 , the weight of the swollen specimen in the second liquid; \underline{p} , the weight of the swollen specimen in vacuum; \underline{V} , the volume of the gel specimen after swelling; \underline{V}' , the volume of one gram of the gel after swelling; $\Delta \underline{V}'$, the maximum relative error in the determination of the volume of one gram of the gel after swelling; $\underline{K}_V = \underline{V}' / \underline{V}_0$, the value of the volume coefficient of swelling.

The maximum relative error $\Delta \underline{V}'$ for each of five parallel determinations of the volume occupied by one gram of gel after swelling, and the maximum relative error \underline{E} , are determined as follows [1]. We have

$$\underline{V}' = \frac{p_1 - p_2}{d_2 - d_1} \text{ ml; } d_1 \text{ and } d_2 \text{ are given}$$

then $\ln \underline{V}' = \ln(p_1 - p_2) - \ln(d_2 - d_1)$.

$$\underline{d} \ln \underline{V}' = \underline{d} \ln (p_1 - p_2); \quad \underline{E} = \frac{\underline{dV}'}{\underline{V}'} = \frac{|\underline{dp}_1| + |\underline{dp}_2|}{p_1 - p_2},$$

$$\Delta \underline{V}' = \frac{|\underline{dp}_1| + |\underline{dp}_2|}{p_1 - p_2} \underline{V}'.$$

As the weighing is to an accuracy of ± 0.3 mg, we have

$$|\underline{dp}_1| + |\underline{dp}_2| = 0.3 \text{ mg.}$$

Then

$$\Delta \underline{V}' = \frac{0.0006 \cdot \underline{V}'}{p_1 - p_2} \text{ ml.}$$

The exact volume occupied by one gram of the gel after swelling is equal to

$$\frac{\Sigma \underline{V}'_i}{5} + \frac{\Sigma \Delta \underline{V}'_i}{5}$$

Then, for this volume, the maximum relative error, expressed as a percentage, is

$$\delta = \frac{100 \Sigma \Delta \underline{V}'_i}{\Sigma \underline{V}'_i}$$

In determinations of the volume of the swollen gel, for Japanese agar, $\delta = 2.2\%$, for white beans, $\delta = 1.4\%$; for rubber, $\delta = 2.5\%$.

The values of the weight coefficient of swelling for these substances are shown in Table 2, where \underline{p}_0 is the weight of the dry gel; \underline{p} is the weight of the specimen after swelling; \underline{K}_p is the weight coefficient of swelling; Δ is the maximum absolute error for each of five values of the weight coefficient of swelling.

The maximum absolute error and the maximum relative error are determined as follows.

TABLE 1

Determination of the Volume Coefficient of Swelling for Japanese Agar, White Beans and Rubber

P_0	V_0'	P_1	P_2	P	V	V'	$\Delta V'$	$\frac{V'}{V_0'}$
Japanese agar, $d_1 = 0.8632$, $d_2 = 1.0167$								
0.0200	0.730	0.0299	0.0032	0.1801	0.1740	8.700	0.1955	11.9
0.0191	0.730	0.0278	0.0020	0.1729	0.1681	8.802	0.2047	12.0
0.0206	0.730	0.0320	0.0032	0.1939	0.1876	9.105	0.1897	12.5
0.0208	0.730	0.0321	0.0043	0.1884	0.1811	8.706	0.1879	11.9
0.0218	0.730	0.0349	0.0056	0.1996	0.1909	8.756	0.1793	12.0
Mean						8.814	0.1914	
Maximum relative error							2.2%	
White beans, $d_1 = 0.8656$, $d_2 = 1.0182$								
0.1196	0.697	0.0641	0.0208	0.3098	0.2838	2.372	0.0329	3.40
0.0953	0.697	0.0505	0.0150	0.2519	0.2327	2.442	0.0413	3.50
0.1213	0.697	0.0654	0.0220	0.3105	0.2831	2.334	0.0323	3.34
0.1342	0.697	0.0723	0.0258	0.3301	0.3048	2.273	0.0293	3.26
0.1429	0.697	0.0788	0.0267	0.3743	0.3414	2.390	0.0275	3.43
Mean						2.362	0.0326	
Maximum relative error							1.4%	
Rubber I, $d_1 = 1.001$, $d_2 = 1.1350$								
0.1491	0.792	0.0190	0.0049	0.1978	0.1786	1.198	0.0299	1.51
0.1470	0.792	0.0196	0.0040	0.1962	0.1765	1.201	0.0304	1.51
0.1470	0.792	0.0187	0.0048	0.1941	0.1753	1.193	0.0304	1.50
0.1518	0.792	0.0195	0.0049	0.2016	0.1819	1.191	0.0292	1.50
0.1425	0.792	0.0177	0.0052	0.1887	0.1710	1.200	0.0314	1.51
Mean						1.196	0.0303	
Maximum relative error							2.5%	

We have $K_p = \frac{p}{p_0}$, then

$$\ln K_p = \ln p - \ln p_0; \quad d \ln K_p = d \ln p - d \ln p_0;$$

$$\frac{dK_p}{K_p} = \frac{dp}{p} - \frac{dp_0}{p_0}; \quad dK_p = \frac{dp}{p_0} - \frac{p dp_0}{p_0^2};$$

$$|dK_p| = \Delta = \left| \frac{dp}{p_0} \right| + \left| \frac{p dp_0}{p_0^2} \right|.$$

As the weighing is to an accuracy of ± 0.3 mg, we have

$$\Delta = \frac{0.003}{p_0} + \frac{0.003p}{p_0^2}.$$

The exact value of K_p is

$$\frac{\Sigma(K_p)_i}{5} + \frac{\Sigma \Delta_i}{5}$$

TABLE 2

Determination of the Weight Coefficient of Swelling for Japanese Agar, White Beans, and Rubber

P_0	P	K_p	Δ
Japanese agar			
0.0200	0.1801	9.000	0.1501
0.0191	0.1729	9.520	0.1579
0.0206	0.1939	9.413	0.1516
0.0208	0.1884	9.058	0.1450
0.0218	0.1996	9.156	0.1400
Mean		9.136	0.1489
Maximum relative error			1.6%
White beans			
0.1196	0.3098	2.590	0.0090
0.0953	0.2519	2.643	0.0114
0.1213	0.3105	2.560	0.0088
0.1342	0.3301	2.462	0.0077
0.1429	0.3743	2.619	0.0076
Mean		2.568	0.0089
Maximum relative error			0.4%
Rubber			
0.1491	0.1978	1.327	0.0047
0.1470	0.1962	1.335	0.0048
0.1470	0.1941	1.321	0.0047
0.1518	0.2016	1.330	0.0046
0.1425	0.1887	1.327	0.0049
Mean		1.328	0.0047
Maximum relative error			0.3%

The maximum relative error δ for the weight coefficient of swelling is 1.6 % for Japanese agar, 0.4% for white beans; 0.3% for rubber.

Let us now compare our method for the simultaneous determination of the coefficients K_V and K_p on the same specimen of gel, with presently available typical methods for determining the volumes of the dry and swollen gel, the weight of the swollen gel, and the coefficients K_V and K_p .

These methods may be divided into the following groups.

A. Determination of the volume of the swollen gel by Fisher's method [2], and modifications of this method. Defects of this method include the difficulty of determining the upper boundary of the gel, as it is uneven and diffuse, especially at high degrees of swelling. The height of a column of swollen gel gives only a relative idea of the extent of swelling, as the height of the gel column cannot be an exact measure of swelling. The reproducibility of the results is from 5 to 10%.

B. Determination of the volume of the dry and swollen gel by Lottermoser's method [3], and modifications of this method. The apparatus of Zhukov [4], Simkhovich [5], Ermolenko and Mazel [6], Tyazhelova [7].

The main disadvantage of such apparatus is the necessity of using mercury, which is associated with a number of difficulties. The surface of the mercury soon becomes

soiled, and after each experiment, it is necessary to wash the mercury and the porous plate thoroughly. Large errors are possible because of the difficulty of establishing the mercury level with complete contact with the porous plate.

C. Determination of the weight of liquid absorbed by the gel during swelling, by Hofmeister's method [8]. The defects of this method are well known. We may also note the apparatus of Dogadkin [9], Ermolenko and Mazel [6], and also Tyazhelova's apparatus [7]. The most accurate is the Ermolenko and Mazel apparatus.

D. Determination of the volume and weight coefficient of swelling simultaneously (with the same specimen) is carried out with Tyazhelova's apparatus [7] and in the method proposed by us. Tyazhelova's apparatus is constructed on the principle of Lottermoser's apparatus; it is fairly fragile and needs to be absolutely air-tight. It is not possible to use a thermostat with this apparatus. The preliminary operations require a great deal of time (to establish the zero point, to measure the volume of the air-dry substance, and to draw the liquid from the pipet into the swelling vessel, requires about 1.5 hours). The volume is measured by means of mercury, which is associated with numerous disadvantages. The maximum relative error in determining the volume coefficient of swelling is 1.5%.

The advantage of our proposed method is simplicity of equipment and rapidity of working. Four to five minutes are necessary to weigh the cups with and without the specimen in the two liquids and to rinse the specimen. The true volume of the swollen gel is determined by this method. The maximum relative error in determining the volume coefficient of swelling is from 1.4 to 2.5%, and for the weight coefficient of swelling it is from 0.3 to 1.6%.

Thus, with the aid of our proposed method it is possible to determine the volume and weight coefficients of swelling simultaneously (with the same specimen of the gel) with sufficient accuracy.

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* See Consultants Bureau Translation, page 421.

COMMENTS ON THE QUESTION OF SURFACE DEMIXING

[Reply to the paper by G. L. Starobinets, I. Z. Fisher, and M. G. Milchina
on "Surface Demixing," Colloid J., 15, 219 (1953)]*

B. Ya Teitelbaum

1. Unfortunately, Starobinets, Fisher and Milchina, instead of dealing with the substance of our papers and carrying out criticisms on a basis of principles, desiring to defend their point of view, preferred to proceed otherwise. They make a number of assumptions, and then "establish" their inconsistency, giving the impression of exposing our errors.

Here, for example, is one of their most important arguments: "since . . . the droplets of the 'surface emulsoid' have microscopic dimensions, which significantly exceed the thickness of the surface layer of the liquid, almost entirely in a region physically forbidden to them." Later the impossibility of this is shown on a thermodynamical basis. All this is true, but our papers deal with surface, two-dimensional demixing, and there is no mention anywhere of droplets which significantly exceed the thickness of the surface layer. Consequently they enter the "forbidden region" entirely because of our critics themselves.

The "example" given in the paper cannot fail to evoke surprise. A solution of methyl alcohol in benzene of 0.5 mole fraction is considered at 20°. The assumption is made that surface demixing occurs in this solution and a surface emulsoid is formed, and then the assumption is proved to be invalid: "The droplets of the imaginary emulsoid have about the same right to existence as ice at 27° at normal pressure in contact with water." Readers may get the impression that Starobinets, Fisher, and Milchina prove us wrong by quoting "chapter and verse."

The fact of the matter is that they understand surface demixing incorrectly. Moreover, the formation of a "surface emulsoid" of methyl alcohol in benzene is their own invention. Let us assume, however, that our critics chose the given system (for the reason that the vapor pressures for it are known [1]) on the view that surface demixing is as improbable in this as in any other system. The authors of the critical paper have apparently forgotten that in demixing two mutually saturated solutions are formed (the vapor pressures of which, incidentally, are equal). They assume that their imaginary "emulsoid of the alcohol in benzene type" contains droplets of the pure alcohol with its own vapor pressure; they propose to compare the vapor pressure of the alcohol over the emulsoid droplet with the partial vapor pressure of the alcohol within the volume of the solution (?!). Although the meaning of this is difficult to understand, it is seen from the cited values that we have here a simple comparison of the vapor pressures of the alcohol alone and in benzene solution (mole fraction 0.5). The first value is certainly greater than the other by 22 mm Hg, but what has this to do with surface demixing?

2. We intend to examine separately the question of the thermodynamic validity of surface demixing. Here we shall draw attention to a strange conclusion, which again shows that our critics did not understand the point. They state that there is no doubt that the duration of our experiments for each solution was of the order of several days (?), and they therefore conclude that the experiments relate to some equilibrium property of the solution, which the formation of a surface emulsoid cannot be. If the authors considered the essence of the matter, they would understand that, by the very nature of the measurements, one can speak of the duration of the experiment in the present case only in the sense of the duration of the existence of the newly formed surface after each separate act of foaming or in the formation of a separate bubble in surface tension measurements. This duration was measured in minutes at the best. Thus, the argument of our critics is meaningless.

3. Certainly it is not admissible to examine the surface phase in isolation from the liquid and gaseous phases of the system; nevertheless it cannot be considered identical with the liquid phase or devoid of definite properties, due mainly to the existence of surface free energy and a definite orientation of molecules at the surface of separation of the liquid and gas phases. Because of this, as is known, the composition of the surface layer in general differs significantly from the composition within the volume of the solutions, and the activity coefficients in the surface layer also differ from the corresponding values within the volume. From this, however,

* See Consultants Bureau Translation, page 223.

follows the possibility, and the thermodynamic necessity in a number of cases, of surface demixing, especially in systems with a tendency to volume demixing. In the light of the above it is quite incomprehensible why peculiarities in the results of surface tension measurements may be due "only to changes in the structure of the liquid within its volume" which occur at the same temperatures, as is considered by Starobinets, Fisher, and Milchina.

4. In the paper in question, the authors correctly state that a decisive proof of surface demixing could only be a direct experiment which confirms the existence of a "surface emulsoid," for example, direct ultramicroscopic observation, or study of the intensity and polarization of light scattered from the surface of the solution, etc. The desirability of such experiments is undoubted. However, if only a direct experiment of this type can be a decisive proof, only such a direct experiment can be accepted as a decisive refutation. As regards dielectric constant or capacity measurements, these evidently cannot serve as such an experiment. Moreover, we cannot regard the data presented in the paper in question as fully convincing.

In Fig. 1 of the paper cited, the deviation of the experimental points from smooth lines is not great, and it is impossible to show objectively the presence of any points of inflexion on them. Comparison of this figure with surface tension data for the same system [2] shows that the shading on the diagram for the dielectric constant does not coincide with the region of surface demixing, as Starobinets and his co-authors assert. A difference of $8-10^\circ$ is too great to escape notice.

Is it possible, on the basis of such experimental material, to assert with certainty that the data of these authors indicate some changes in the volume structure of the liquid at temperatures which correspond to the anomalies in surface tension measurements observed by us? This material appears to us to be clearly inadequate. However, even if this correlation were proved, it could not serve as a refutation of the concept of surface demixing. Indeed, such observations would help to determine a relationship between surface-volume effects, the latter of which in some sense causes the former. But they cannot make it possible to decide whether the surface layer of the systems in question is homogeneous or heterogeneous.

5. Starobinets, Fisher and Milchina consider that the effects observed by us in our polythermic study of surface tension are essentially identical with the effects previously discovered and systematically studied by S. S. Urazovsky [3] and Semenchenko [4]. Let us examine the extent to which this view is correct.

Since the effects found by Urazovsky and co-workers on the polytherms of surface tension [5] (and of a number of their properties) are associated with interconversion of molecular forms [6], the corresponding effects in our solutions might be attributed to molecular polymorphism of the components and might in the first instance be reflected in the surface tension polytherms of the components. Nevertheless, in all the systems studied the anomalies always appeared only in solutions, and particularly clearly in the region of medium concentrations. But then it follows from this, and from a number of other considerations which cannot be dealt with here, that there is no basis for seeking an explanation of the effects observed by us in studies of surface tension and foam formation in the light of the theory of molecular polymorphism, as is recommended to us by Starobinets, Fisher and Milchina.

As regards their other recommendation, according to which our observed facts should be examined in the light of Semenchenko's views on the mechanism of generalized critical phenomena, this appears to us quite logical. Since we hold the view that surface demixing takes place in the solution, its laws should be described by Semenchenko's theory. In particular we should note the fluctuating nature of the process of new phase formation and of the transition of the substance near the critical point (point of demixing) into the disperse state. We put forward this view publicly in 1950 at the Conference on Physico-Chemical Analysis during the discussion of Semenchenko's paper [7]. We examined our observed facts as a peculiar form of critical phenomena and saw in them a new confirmation of the views of Semenchenko.

However, it is not possible to decide on the basis of the generalized theory of critical phenomena only, whether the critical effects discovered by us relate to the surface layer or the volume of the solution.

6. The question of the relation of surface demixing to foam formation deserves serious attention. The facts cited in our papers show that with the aid of the concept of surface demixing it is possible to explain a number of effects in the formation and stability of foams, although at the present time it is difficult to put forward a mechanism of foam stabilization in the cases studied. In any case, formation of more or less stable foams was always observed in systems for which we postulated surface demixing on the basis of surface tension measurements.

We certainly do not disagree with Starobinets, Fisher and Milchina that the stability of foams in the systems studied may be explained by the properties of the adsorptional layers on the solution-air boundary. (Possibly these authors oppose this viewpoint to their distorted concept of "surface demixing" according to which disperse formations arise outside the surface layer). We understand surface demixing to be a property of the adsorptional layer.

Unfortunately, within the limits of a short discussion it is not possible to give detailed consideration to all the points touched upon in the paper in question. Let us, however, sum up certain conclusions.

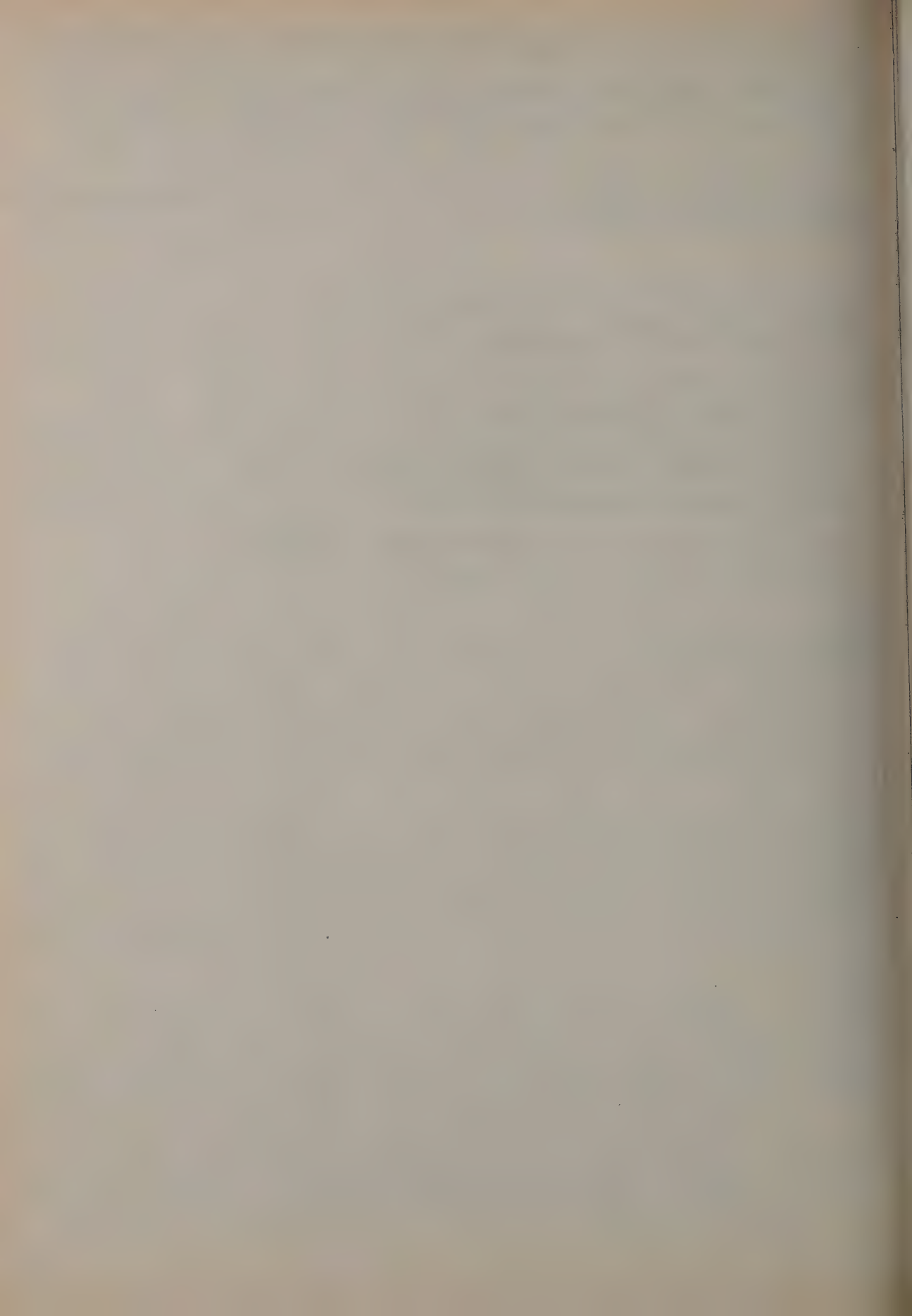
Starobinets, Fisher and Milchina did not put forward a single valid contradiction to the concept of surface demixing, and their arguments are based on a preconceived notion; they are evidence of a superficial acquaintance of our papers and a reluctance to consider the essence of the matter; they do not stand up to criticism.

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FURTHER TO THE SUBJECT OF SURFACE DEMIXING

(Reply to B. Ya. Teitelbaum's

"Comments on the Question of Surface Demixing")

G. L. Starobinets

In the paper cited above, the author admits that his published papers do not contain experimental proofs of the existence of surface demixing.

Since B. Ya. Teitelbaum continues to believe that we did not produce a single valid objection to the concept of surface demixing, we are compelled to return once again to a very brief theoretical examination of the question within the framework of thermodynamics.

B. Ya. Teitelbaum's system consists of two coexisting surface phases in contact with a homogeneous volume solution. Let us assume that we wish to calculate the surface tension of this system, for example, with the aid of Zhukhovitsky's equation:

$$\sigma = \sigma_1 + n_0 RT \ln \frac{b_1}{a_1}$$

where σ is the surface tension of the solution; n_0 is the relative number of moles of the first component in the surface layer; b_1 and a_1 are the activities of the first component in the surface layer and in the volume respectively. The transition from the activity of the first component in the volume to the activity in the surface layer is possible with the aid of the curve for the composition of the surface layer against the composition of the volume solution. But in B. Ya. Teitelbaum's system there are two such curves for two coexisting surface phases; consequently, we should obtain two series of surface activities and two surface tension isotherms, one of which, corresponding to the imaginary surface phase, has no validity. B. Ya. Teitelbaum's system leads to this contradiction because it ignores one of the fundamental postulates of modern thermodynamics of surface phenomena: all the properties of a surface layer in a direction parallel to the surface of separation should be homogeneous. Hitherto B. Ya. Teitelbaum ignored this without any theoretical basis, but in Section 2 of the preceding article he promises to publish considerations which refute this postulate. Until the new thermodynamical views of B. Ya. Teitelbaum are published, we refrain from a more detailed examination of this question.

It should also be remembered that despite the inequality of composition between the surface layer and the volume of the solution, the chemical potentials of any component in the surface layer and in the volume are equal because the surface layer is under a tension equal to the surface tension. If, in B. Ya. Teitelbaum's surface layer, we imagine ourselves moving along the surface of separation (obviously with the composition of the volume solution constant), we meet regions of different composition, and therefore under different tensions. The unreality of such a surface layer is obvious. Therefore, B. Ya. Teitelbaum's attempts to prove the contrary are futile.

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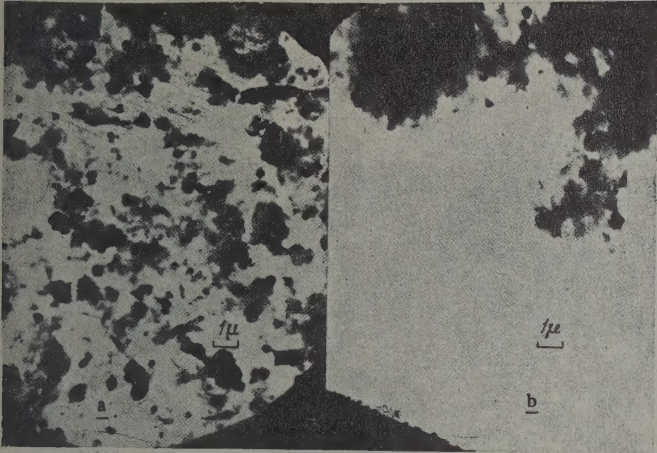


Fig. 4. Electron microscope photographs of peat water with a dry content of 0.113%. a) Original; b) coagulated suspension.

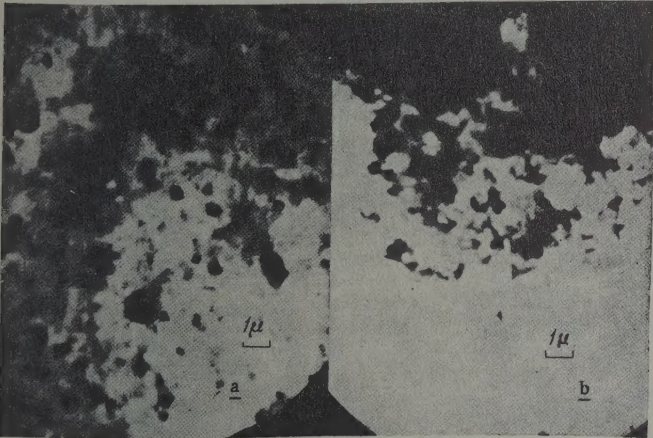


Fig. 5. Electron microscope photographs of peat water with a dry content of 0.076%. a) Original; b) coagulated suspension.

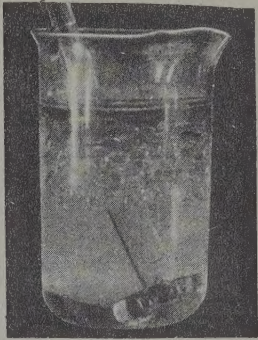
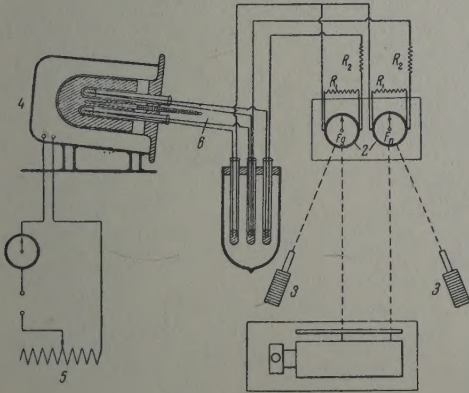


Fig. 1. Formation of emulsion during stirring with a glass plunger.

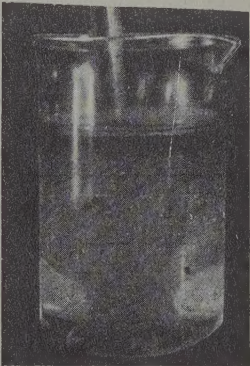


Fig. 2. Formation of emulsion during stirring with a plastic plunger.

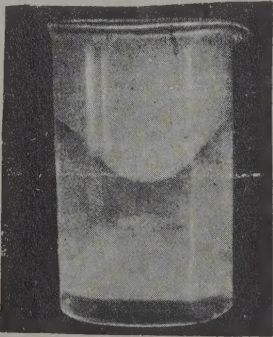
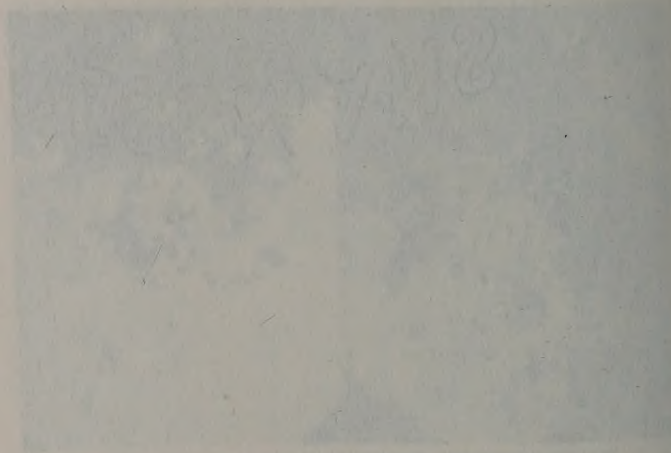
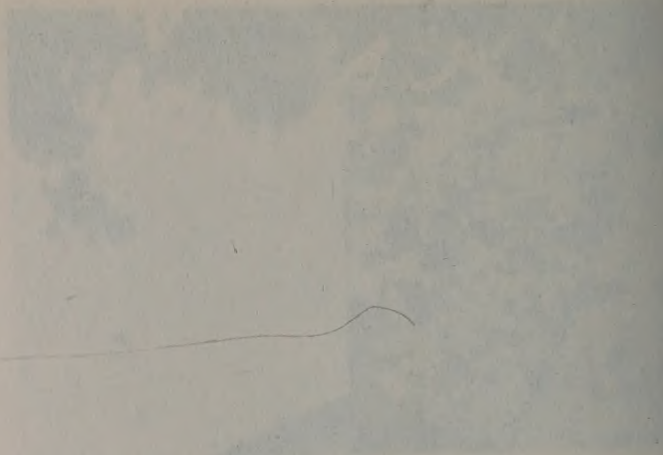
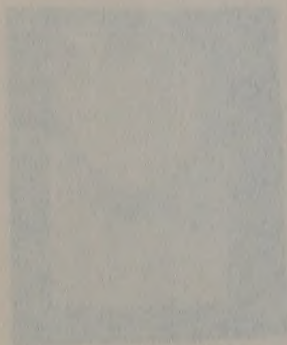
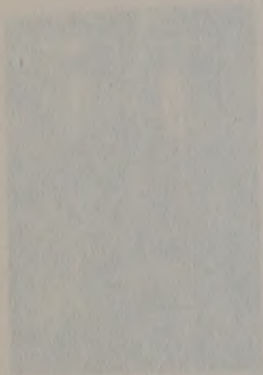


Fig. 3. w/o Emulsion of transformer oil and oil well water.

Fig. 1. Pyrometric apparatus scheme (explanation in text).



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